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Second Interim Report: Quality Assurance Support for the National Atmospheric Deposition Program and National Trends Network Monitoring Activities: 1987-1990

Grant Number CR813910-03

David S. Bigelow

NADP/NTN Quality Assurance Manager
Natural Resource Ecology Laboratory
Colorado State University
Fort Collins, Colorado

Project Officer

Berne I. Bennett
Quality Assurance Division
Atmospheric Research and Exposure Laboratory
Research Triangle Park, North Carolina 27711

ATMOSPHERIC RESEARCH AND EXPOSURE LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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This report summarizes the quality assurance activities of the NADP/NTN Quality Assurance Manager from mid-1988 through mid-1989. The report presents some accomplishments and makes recommendations for the network.

The report outlines the progress being made by the NADP/NTN monitoring program in completing documentation of standard operating procedures, responding to field operation and siting deficiencies and discusses data quality issues relating to the handling of trace samples and the quality coding of daily rain amounts. The report also contains an evaluation of a second laboratory's participation in the network and reports on a preliminary evaluation of Nipher-shielded Belfort rain gage performance in the network.

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SECTION 1
INTRODUCTION

Background

The National Atmospheric Deposition Program (NADP) monitoring network began operations in July of 1978. The network used, and continues to use cooperating local, state and federal agencies as well as private industry to operate a network of sites according to a single set of protocols. In 1983, NADP assumed responsibility for managing the day-to-day operations of the National Acid Precipitation Assessment Program's National Trends Network (NTN). This action resulted in the combined, cooperative monitoring program now known as the NADP/NTN monitoring network (Cowling et al., 1977; NADP, 1978; Interagency Task Force On Acid Precipitation, 1982; Robertson and Wilson, 1985). The NADP/NTN monitoring network serves both the National Atmospheric Deposition Program and the National Acid Precipitation Assessment Program.

Because the NADP/NTN monitoring program both represents and relies on many different public and private agencies to accomplish its goals, it is unique in its structure and mode of operation (NADP, 1984). For quality assurance, this has meant that responsibility for the development of quality assurance programs has been and continues to be a voluntary effort assumed by each of the agencies who have responsibility for managing specific pieces of the network operations (i.e field sites, Central Analytical Laboratory, Coordination Office, U.S. Geological Survey, U.S. Environmental Protection Agency). These quality assurance procedures are then reviewed and accepted by the various NADP committees who have responsibility for overseeing each network function. This practice has been strongly encouraged since it would require considerable effort and expertise to centralize this function within a single organization.

A decentralized approach to quality assurance, however, creates its own problems. Many of the network quality assurance procedures are innovative adaptations of recognized quality assurance practices, and as such are reported in scientific literature, at professional and technical meetings or in various agency reports rather than in a standard network document or operating procedure publication (see Selected Publications). This lack of centralized quality assurance reporting makes documenting the achievement of network data quality goals and objectives difficult and also makes it difficult to continue some key quality assurance programs once scientific recognition for the techniques has been achieved. The likelihood that those quality assurance activities that cannot be maintained by a single agency, either because of financial or cooperative restraints, will be overlooked is also increased. Finally, decentralized reporting can lead to situations where results from one effort may conflict with another such that no clear picture of 'true' data quality can emerge.

Recognizing the need for a more coordinated and thorough quality assurance program, NADP formed a study committee in 1982 to address this issue. The work of this committee resulted in the development of a Quality Assurance Plan (NADP, 1984) to cover all aspects of network operation and the recommendation that a full time Quality Assurance Manager be appointed to administer this quality assurance program. The desirability of a coordinated quality assurance program was again recognized in the NAPAP Peer Review held in Boulder, Colorado in 1985 (Joyner, 1986).

Objectives

The purpose of the cooperative agreement, *Support to the National Atmospheric Deposition Program/ National Trends Network Quality Assurance Program*, contract number CR813910-03, is to provide ongoing support for the NADP/NTN Quality Assurance Manager. The QA Manager coordinates the quality assurance activities of the joint NADP/NTN monitoring network, identifies and develops new quality assurance programs for the network as necessary, and reports on the quality of deposition data being produced by the NADP/NTN monitoring effort.

It is the responsibility of the Quality Assurance Manager to administer the NADP Quality Assurance Plan that was adopted by the NADP program in 1984. This requires the manager to maintain close liaison with the Central Analytical Laboratory; the U.S. Geological Survey's external NADP/NTN audit programs; the data management and publication activities of the NADP/NTN, as administered through the Coordinator's Office; the EPA's Site Visitation Program and Acid Deposition System for Statistical Reporting (ADS); and to establish a program to monitor the activities at each of the deposition monitoring stations. The QA Manager also works closely with the QA Steering Committee and provides necessary information to appropriate NADP and NAPAP Task Group IV committees. The Manager is independent of other program operations, such as network site operations, chemical analysis, data management and publication.

The primary objectives of the Quality Assurance Manager are to:

1 Oversee the implementation of the NADP Quality Assurance Plan.

2. Review and recommend changes to the NADP/NTN monitoring network's field operations, laboratory operations, data management and external quality assurance programs and activities.

3. Identify and evaluate the type, level, and effectiveness of the quality assurance procedures in each phase of the program.

4. Report the results of these evaluations.

5. Provide centralized documentation of the quality assurance activities, both internal and external, to the program.

6. Troubleshoot the weaknesses and future needs of the NADP/NTN quality assurance program; take action to correct the problems and meet the future needs of the program.

7. Maintain and prepare documents outlining the details of the NADP/NTN quality assurance procedures.

SECTION 2
ACCOMPLISHMENTS

Coordination of NADP/NTN Quality Assurance Plan Implementation

As in previous years the primary coordination efforts of the Quality Assurance Manager have involved attending the frequent NADP Technical and Subcommittee meetings; writing, revising and reviewing NADP/NTN documentation; reviewing agency reports and proposals that utilize NADP/NTN data or documentation; and disseminating quality assurance information to the various NADP committees and scientists. Each of these activities serves as a vehicle for obtaining and documenting the quality assurance activities of the network and for promoting the evaluation and reporting of quality assurance data.

Two areas of coordination activities received special attention during this past year. These activities were the staffing of a new site liaison in the NADP/NTN Coordination Office and the drafting and review of standard operating procedures identified as missing during the revision of the NADP/NTN Quality Assurance Plan.

Other tasks undertaken by the Quality Assurance Manager as a part of the coordination task included: 1) the participation by the Quality Assurance Manager in *adhoc* committees to complete a formal procedure for comparing analytical methods (See Section 5), and to review the development of a training video for NADP/NTN Site Operators and Supervisors (Copies available through the NADP/NTN Coordination Office); 2) the completion of an ASTM standard for choosing locations and sampling strategies; and 3) participation in a review of a newly instituted collocated collector program sponsored by the USGS. The Quality Assurance Manager also assisted in the training of USGS personnel and in the locating of candidate sites for the program.

Coordination Office Site Liaison

The Quality Assurance Manager oversees the Site Visitation Program and provides administrative assistance to the program's auditors. The Quality Assurance Manager is also responsible for distributing the results of the site audits and for initiating corrective action when any deficiencies are discovered. The program involves four auditors who, in the past, reported results to the Quality Assurance Manager. The Quality Assurance Manager then entered the data into the NADP/NTN data system, reviewed the reports and attempted to initiate remedial actions as necessary. Because most sites required some form of follow-up action, and previous audits conducted prior to 1984 had not been responded to, considerable effort is required to bring each of the now 200^{+} sites into siting and performance compliance. In addition, similar data entry, review and action is required by the Quality Assurance Manager in the Blind-Audit, Intersite Comparison and Interlaboratory quality assurance programs sponsored by the U.S. Geological Survey; in independent audits and reviews conducted by the Quality Assurance Manager as a part of his troubleshooting and future needs assessment duties; and NADP Subcommittee activities. As might be expected with a single, three-quarters time position, many noted audit deficiencies were not being acted upon in a timely manner.

In November of 1988, the NADP/NTN Coordination Office was authorized to staff a Site Liaison to assist in the data entry, review and follow-up of Site Visitation Program results. The Quality Assurance Manager has assisted in defining the duties and responsibilities of this position and in the training of the person chosen to fill the position. This has included reviewing and revising responses to siting deficiencies and in evaluating new and proposed changes to siting locations. Unfortunately the original person occupying the position resigned after only eight months. As a result the selection and training efforts had to be repeated. Training activities for this new employee will continue into the next calendar year.

Documentation

Efforts to improve the documentation of standard operating procedures used in the network were accelerated after the Quality Assurance Manager identified 13 documents that would be required to complete the data management portion of the NADP/NTN Quality Assurance Plan revision (See below). The importance of these and other network documentation was given further attention with the initiation of NAPAP's state of science activities and by a review of a second laboratory's brief involvement in network laboratory operations (See Section 6).

As a result of efforts by the NADP/NTN Coordination Office, the Central Analytical Laboratory and the U.S. Geological Survey, 22 documents representing more than 800 pages of text have been produced which detail various operating procedures used by the network to gather, evaluate and disseminate network samples and data. All of the documents are in various stages of draft and review and will require many more man hours of editing before they can be put into final form. However, even in draft form the documents represent significant progress towards the completion of network documentation.

The Quality Assurance Manager has been involved in the production of many of these documents as a reviewer, an author and as a source of network information. It is expected that much more of the Quality Assurance Manager's time will be required to continue this review and to assist in the completion of these documents. Titles, authors and agency affiliations are included in the listing of references given later in this section (See **Centralized Documentation and Quality Assurance Reporting**).

Review and Evaluation of NADP/NTN Network Operations

Three areas of Network operations were targeted for review during the past contract year by the Quality Assurance Manager. The reviews covered an evaluation and recommendation for integrating data from a second laboratory into the network data system, an evaluation of a Nipher-shield modification to the standard rain gage used by the network as a way of improving rain volume measurements made by the network, and an evaluation of unpublished NADP/CANSAP network co-location activities. The reviews resulted in two reports[1] [2] (See Sections 6 and 7), the presentation of one poster at the NADP Technical Committee Meeting held in Provincetown, MA in October of 1989[3] and the initiation of two journal articles[4] [5].

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1 BIGELOW, D.S. 1989. The Integration of Monitoring Data from a Second Laboratory Into The NADP/NTN Data System. Report to the NADP Technical Committee September 1989.

2 Simmons, C.L; BIGELOW, D.S. 1989. Progress Report: Comparison of Precipitation Measurements from Collocated Nipher-Shielded and Standard Rain Gages at NADP/NTN Sites. Report made to the Environmental Protection Agency, November 1989.

3 Simmons, C.L; BIGELOW, D.S. 1989. Comparison of Precipitation Measurements from Collocated Nipher-Shielded and Standard NADP/NTN Rain Gages - Preliminary Results. Poster, 1989 NADP Technical Committee Meeting, Provincetown, MA. Abstract: National Atmospheric Deposition Program, NADP Technical Committee Meeting: Abstracts of Papers, Provincetown, MA. October 23-26, 1989 Colorado State University, Fort Collins, CO, October 1989.

4 BIGELOW, D.S; Denning, A.S; Baron, J. Differences Between Nipher and Alter Shielded Rain Gages at Two Colorado Deposition Monitoring Sites. Submitted to
Environmental Science and Technology

5 BIGELOW, D.S. Comparability of Wet-Only Precipitation Chemistry Measurements From the United States' National Atmospheric Deposition Program (NADP) and the Canadian Network For Sampling Acid Precipitation Program (CANSAP). To be submitted to Atmospheric Environment

Evaluation of the Second Laboratory in the NADP/NTN monitoring program

Site liaison and chemical analyses of samples from 18 NADP/NTN monitoring sites administered by the National Park Service were performed by a second laboratory from March 24 through September 29, 1987. At the request of the NADP Subcommittee on Network Operations the Quality Assurance Manager was asked to determine the comparability of the second laboratory's data to that of the Central Analytical Laboratory. The evaluation concluded that chemistry data are not of the same quality as previous and subsequent NADP/NTN data. Detection/reporting limits are not comparable, precision is not comparable and unresolved problems with sulfate analyses and ion balances render the data questionable. Field measurements, however, gathered and screened by the second laboratory and re-evaluated by the Illinois State Water Survey can be used 'transparently' with other similar data gathered by the network.

Recommendations for the integration of this information into the NADP/NTN data system include the coding of the second laboratory's data to identify it as originating from a laboratory other than the Central Analytical Laboratory, the integration of field data into the standard data base, the entering of the laboratory data into a special data base and the sequestering of all laboratory chemical analysis data from all but very special requests. A copy of the report which is reproduced in Section 6 is to accompany all requests for data from the second laboratory.

Nipher Shield Evaluations

In 1987, the U.S. Environmental Protection Agency began a comparison of a Nipher-shielded Belfort rain gage to the standard Belfort rain gage used by most deposition monitoring programs in the United States. The study utilizes nine NADP/NTN atmospheric deposition monitoring sites chosen to represent a variety of snow collection conditions that might be found within existing national deposition monitoring programs. Favorable results taken from deposition monitoring sites, primarily in northeastern North America, have prompted the U.S. Environmental Protection Agency and the Electric Power Research Institute to adopt the Nipher gage as a standard piece of equipment in the Acid MODES and Operational Evaluation Network monitoring programs, and to propose that it be included as a standard gage in other North American deposition monitoring programs such as the NADP/NTN network.

Because the data collected in the study was not being analyzed and because the conclusions of the study will have a direct bearing on the quality of previous precipitation measurements made by the NADP/NTN network and may change the standard basis for determining the representativeness of collector volumes (catch efficiency) used in the network, the Quality Assurance Manager became concerned that the precipitation measurement standard used by the network would be changed without benefit of the results of this important study.

A report, to be submitted to the U.S. Environmental Protection Agency gives inconclusive results for weekly and daily precipitation amount data sets from paired Nipher-shielded and standard Belfort rain gages at 8 sites (one site only recently became operational). In general, all of the sites showed higher values for Nipher-shielded rain gages for snow, rain and mixed types of precipitation. The differences ranged from negligible amounts up to 37% of the volume for snow at one site. In weekly data sets, statistically significant differences occurred at only five of the eight sites when all precipitation types (rain, snow, mixed) are analyzed together and in only two of the sites when snow was analyzed separately. Rain was significantly different at three of the sites. Daily data was analyzed at only two sites but in general supported the conclusions drawn from the weekly data. One site showed significant differences for rain and snow and the other site did not.

The study is scheduled to be completed after another year of data has been gathered. The extra year's data is needed to increase the number of usable samples. Sample numbers have

been affected by the drought conditions in much of the western United States. The final report should also contain a more complete analysis of the the daily data sets from each of the sites. A draft of a paper outlining the results of the daily data at two sites has been prepared for submission as a journal article.

US/Canadian Intercomparisons

Beginning in 1981, the National Oceanic and Atmospheric Administration (NOAA) sponsored a three-year, direct comparison of atmospheric deposition monitoring protocols used by the National Atmospheric Deposition Program (NADP) and the Canadian Network for Sampling Acid Precipitation Program (CANSAP). The purpose of the comparison was to determine if data from these two networks, could be used as a single data set to characterize atmospheric deposition in North America. Preliminary examination of the data during the study revealed serious contamination problems with much of the CANSAP data. Because no final report was ever made and because the results of the comparison still have value for long-term trend analysis and network introspection, the Quality Assurance Manager was asked to complete the analysis of the comparability study.

Preliminary conclusions derived from an analysis of the complete data set are 1) that the previously noted contamination in CANSAP data may only be a serious problem at unsheltered or locally source rich sites (e.g. poorly sited in regards to local or line sources of emissions) and 2) that the differences at the more rural, emission source-deficient locations exhibit quite similar results. It was noted however, that CANSAP values in general are consistently higher than values from the NADP network. The differences appear to be significant, though at only some of the locations. A revised draft of the paper should be ready for submission to a journal this winter.

Review and Revision of the NADP/NTN Quality Assurance Plan

During October of 1986 the NADP Quality Assurance Steering Committee began the task of reviewing and revising the NADP Quality Assurance Plan. The Quality Assurance Manager had been given the responsibility for the revision of the Data Management portion of the Plan. This portion was completed in August of 1988. More recently the Quality Assurance Manager was given responsibility for developing another portion of the plan detailing the integrated assessment of quality assurance results. No effort was put into this task pending action by others to complete drafts of other portions of the plan. Completion of a working document has been postponed until the spring of 1990.

Troubleshooting the Weaknesses and Future Needs of The NADP/NTN Monitoring Network

Topics related to the data management activities in the network commanded most of the troubleshooting and future needs activities of the Quality Assurance Manager during the previous year. The NADP/NTN Coordination Office began upgrading a number of computer programs and software packages to improve the processing of incoming network data. Rules for identifying and reporting trace samples in the monitoring program were examined after inconsistencies in their handling were identified. A strawman for the screening and quality coding of daily rain values was developed in response to the networks lack of quality control on the processing of daily rain data and finally the Quality Assurance Manager assisted in the organization of two symposia to examine the spatial and temporal data reporting practices of the program.

Data Management Improvements

Data Management activities in the Coordination Office have increased steadily both in size and complexity ever since the monitoring program began. As part of the ongoing effort to reduce the lag in data reporting and the complexity of the data management activity, computer programs, along with software and hardware, have required constant tuning. This has been especially true in the more recent years as many of the NADP/NTN program cooperators began developing and improving their methods of gathering, processing and distributing data. When, for instance, the CAL develops improved data screening algorithms and improves upon the amount and type of information passed along to the Coordination Office, the Coordination Office must update its data handling programs and data base design to accommodate the new or improved information. These tasks are also further complicated by the NADP policy of implementing improvements in data screening and coding retroactively throughout its data set. The importance of applying these improvements retroactively is one of the many unique features of the NADP program which helps to maintain the overall integrity of the NADP data set.

In the past year incoming data handling programs were reviewed in an attempt to streamline data processing of weekly NADP data and to reduce the level of complexity in the programs and data base design required to process and manage this information. As a result of this review the NADP data base design was modified to include more tables and data quality fields in existing tables. Computer programs are also in the process of being rewritten to take advantage of new programming philosophies. As a part of this upgrade, the SUN computer operating system was upgraded from a Release 3 to a Release 4. A future upgrade of the Ingres Relational data base system from Release 5 to 6 is also anticipated. The Quality Assurance Manager has been involved with the planning, upgrading, and quality assurance testing of the programming and software changes.

Identification and Handling of TRACE Samples

The NADP/NTN monitoring program has agreed to code weekly precipitation totals as TRACE when the weekly precipitation total is the result of wet deposition only; is not the product of dew, frost, fog or other types of condensate; and represents an amount of precipitation that is below the detection limit of the sampling system. To implement this philosophical definition, the network is forced to use a number of operational definitions to identify trace samples in its field, laboratory and data management operations. The methods are not always directly comparable and become somewhat subjective and confusing at best when the network attempts to differentiate TRACE samples from non-precipitation events and estimate 'true' sample volumes and rain fall amounts. At the time of the original analysis of the problem over 21 different cases were identified that would have to be considered to correctly process TRACE samples.

At the April 1989 joint Network Operations and Data Management and Analysis Subcommittee meeting the Quality Assurance Manager made three recommendations for improving the handling of TRACE samples in the NADP/NTN monitoring program (See Section 7). The recommendations were intended to clarify and make consistent the handling of TRACE samples in the network. The proposal affected approximately 3000 samples out of the entire NADP/NTN data set collected to date and resulted in a overall net loss of 424 cm in precipitation amounts for the 10-year, 200-site data base. About 44% of the sites displayed an increase in precipitation amounts while the other 54% experienced decreases. It is anticipated that the change in the handling of TRACE samples will result in a less than 2% change in deposition values at all sites on average.

Two of the proposed changes have been adopted by the NADP Technical Committee. The third recommendation has been tabled pending a review of the costs involved in making the publication changes specified in the recommendation. The three recommendations included: 1) allowing site operators to use all means available to them to estimate the occurrence of and amount of volume associated with daily or weekly TRACE samples; 2) the use of the AeroChem Metrics bucket volume as the official weekly precipitation amount for the purposes of data summaries that span multiple NADP/NTN sampling weeks when TRACE samples (defined as those below 0.05 inches on the Belfort and 70 grams of bucket volume) have been recorded; and 3) the separate reporting of weighted averages and volumes in annual summaries for all samples of less than 70 grams bucket volume that are recorded as less than 0.05 inches on the Belfort AND that have chemistry values.

Data Quality Coding of Daily Rain Values

The NADP/NTN monitoring network has as a matter of policy attempted to code rather than sequester data in instances where network protocols have not been followed exactly. Coding, rather than sequestering, provides users of network data with both a maximum amount of information and a highly qualified data set. For daily rain values, however, this practice was ignored. This was in part due to the emphasis the network placed on weekly totals rather than on daily amounts and the fact that the network would accept volume amounts from the AeroChem Metrics Wet/Dry collector in lieu of 'good' rain gage measurements as an acceptable rainfall amount for a weekly total. Common practice in the network was to code as missing daily rain values from network records when problems with the rain gage were detected. In the mid-80's the practice of coding the samples as missing was greatly curtailed, however, this has led to the maintenance of non-qualified daily rain records in the network data base.

To begin the process of quality coding daily rain values in NADP/NTN data records the Quality Assurance Manager proposed a minimal set of guidelines for the network to follow (Section 8). The guidelines were presented to the Data Management and Analysis Sub-Committee in April 1989 and are currently being reviewed by that committee.

Symposiums on the Spatial and Temporal Analysis of Wet-Deposition Data

The spatial analysis of wet deposition and the publication of contour maps that depict concentration gradients of precipitation chemistry is fast becoming a common technique for estimating chemical species concentrations in areas where no monitoring data are available. The NADP/NTN program has for a number of years used contouring maps to summarize and feature NADP/NTN data in its publications. With the increased use of the maps and the renewed interest in the scientific community for improving the current spatial estimation techniques, it was appropriate for the program to re-evaluate the mapping products it was using to display network data.

To provide a background for a discussion of these mapping techniques, the Quality Assurance Manager co-organized a symposium on the spatial analysis of wet deposition. The one-day symposium was held in conjunction with the 1988 NADP Technical Committee meeting held in Champaign, IL October 27-28. The symposium drew approximately 60 scientists and policy makers who were involved in the development or application of spatial analysis techniques for deposition estimation and other geostatistical applications. Conclusions of the symposium were that most spatial mapping techniques, if used correctly, give similar results and that it is only the estimates of uncertainty produced by the different techniques that are different.

Because of the success of the spatial analysis symposium and the need for a similar examination of temporal trend analyses, the Quality Assurance Manager was asked to help with the organization of a temporal trends symposium. Part of his task included the assembling of a 16

site, long-term (10 year), quality assured data set to be used for a comparison of temporal trend techniques. This symposia drew about 40 scientists and policy makers and featured a number of modern techniques that may be used to analyze temporal trends in atmospheric deposition data.

Centralized Documentation and Quality Assurance Reporting

The Quality Assurance Manager's Office continues to serve as a repository for NADP/NTN Monitoring Network documentation. Both internal and external quality assurance information is received and evaluated as a part of the network's documentation. A 1986 quality assurance report on laboratory operations was published by the network during this past contract period and 1987 and 1988 reports of laboratory operations are currently under review. Other new titles noted include:

Brooks, M.H., Schroder, L.J. and Willoughby, T.C., 1988. *Results of External Quality-Assurance Program for the National Atmospheric Deposition Program and National Trends Network during 1985.* Water-Resources Investigations Report 87-4219, U.S. Geological Survey, Denver, CO. p. 14.

James, K.O.W., 1988. *Quality Assurance Report: NADP/NTN Deposition Monitoring, Laboratory Operations, Central Analytical Laboratory, 1986.* National Atmospheric Deposition Program. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO. October 1988. p. 78.

See, R.B., Schroder, L.J. and Willoughby, T.C., 1989. *External Quality-Assurance Results for the National Atmospheric Deposition Program and National Trends Network during 1987.* Water-Resources Investigations Report 89-4015, U.S. Geological Survey, Denver, CO. p. 16.

See, R.B., Schroder, L.J. and Willoughby, T.C., 1989. *A Quality-Assurance Assessment for Constituents Reported by the National Atmospheric Deposition Program And National Trends Network.* Atmos. Environ. 23 (8) pp 1801-1806.

Willoughby, T.C., See, R.B. and Schroder, L.J. 1989. *Stability of Nitrate-Ion Concentrations in Simulated Deposition Samples used for Quality-Assurance Activities by the U.S. Geological Survey.* Water-Resources Investigations Report 89-4042, U.S. Geological Survey, Denver, CO. p. 15.

Other documentation noted but still in draft form include:

Computer Hardware and Programs, Procedures and Software used by the NADP/NTN/CAL Data Management Group. September 1989. The Central Analytical Laboratory.

Field Measurements of NADP/NTN Samples. April 1989. The Central Analytical Laboratory.

Operational Procedures for Archiving NADP/NTN Data and Information at the CAL. September 1989. The Central Analytical Laboratory.

Operational Procedures for the CAL Field Operations Course for NADP/NTN Site Personnel. September 1989. The Central Analytical Laboratory.

Operational Procedures for the CAL Blind Audit Program by the CAL Data Quality Control Officer. September 1989. The Central Analytical Laboratory.

Operational Procedures for the Final Review of NADP/NTN Data by the CAL Data Quality Control Officer. September 1989. The Central Analytical Laboratory.

Operational Procedures for the Initial Review of NADP/NTN Data by the CAL Site Liaison. September 1989. The Central Analytical Laboratory.

Operational Procedures for the Management of the NADP/NTN/CAL Data Bases by the CAL Data Base Manager. September 1989. The Central Analytical Laboratory.

Operational Procedures for the Receipt and Check-In of NADP/NTN Samples at the CAL. September 1989. The Central Analytical Laboratory.

Procedures for Determining Analytical Method Comparability at the Central Analytical Laboratory. October 1989. NADP Sub-Committee for Network Operations.

Procedures Manual: Coordination Office Equipment Depot (COED). September 1989. The NADP/NTN Coordination Office.

Procedures Manual: Intersite Comparison Program. July 1989. The NADP/NTN Coordination Office.

Procedures Manual: Lid Seals. July 1989. The NADP/NTN Coordination Office.

Procedures Manual: NADP/NTN Blind-Audit Program. July 1989. The NADP/NTN Coordination Office.

Procedures Manual: NADP/NTN Isopleth Maps. September 1989. The NADP/NTN Coordination Office.

Procedures Manual: NADP/NTN Semiannual Data Reports. September 1989. The NADP/NTN Coordination Office.

Procedures Manual: Processing of NADP/NTN Site Visitation Information. September 1989. The NADP/NTN Coordination Office.

Procedures Manual: Routine Special Requests. June 1989. The NADP/NTN Coordination Office.

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SECTION 3
RECOMMENDATIONS

The Quality Assurance Manager should continue to actively participate in the various NADP committees and in scientific organizations involved in deposition research. By participating as an active member of these committees and organizations the Quality Assurance Manager is able to stay informed of the many ongoing activities that may have profound impact on the NADP/NTN monitoring program. Committee participation also affords the Quality Assurance Manager with the opportunity to participate in the design, modification and analysis of monitoring techniques and methods early in the life of an agencies or organizations project.

- The Quality Assurance Manager's participation in auditing, document reviews and scientific meetings should continue to be supported. These are the windows through which the Quality Assurance Manager can view the network operations.

The standard operating procedures, quality assurance reports and other selected agency and peer publications that are beginning to document data quality should continue to be gathered and indexed. The integration of external quality assurance data into the main NADP/NTN data system is beginning to allow this data to be published simultaneously along-side monitoring data and to allow peer reviewed assessments of network data quality. Recent publications by Artz et al. 1989; Bigelow et al. 1989; and See et al. 1989 are all examples of the type of data quality assessments that can be made when quality assurance information is made generally available. Unlike agency publications, which typically document the quality assurance activities of a single agency or program, peer-reviewed, integrated reports increase the likelihood that data quality estimates will be appropriate to data use. They also demonstrate how quality assurance information can be used and guide the network in the selection of QA information that is of use to the scientific community.

- The Quality Assurance Manager should continue to evaluate, document and support network data quality and network procedures through the publication of integrated quality assurance reports. These reports should be inclusive of all years of operation through current time.
- Increased support should be made available to expand and accelerate the gathering and data banking of both external and internal quality assurance data that relate directly to the NADP/NTN data set and to allow the timely review and completion of network documentation activities.

One three-quarter time position is not adequate to maintain working relationships with the five primary agencies, two programs (NADP and NAPAP) and numerous committees involved in network quality assurance activities, and, still respond to quality assurance identified deficiencies, organize and evaluate each of the network's quality assurance programs and data, and, produce integrated introspective quality assurance reports and recommendations. Projects, such as the revision of the NADP Quality Assurance Plan (now two years behind schedule) cannot be completed without extensive committee action at the current staffing level.

- Staffing levels should be increased to allow for a full-time Quality Assurance Manager and other support staff. Increased staffing would improve the frequency of integrated quality assurance reports and allow for continuity in the tracking of network quality assurance activities. The current three-quarter time staffing level provides only enough resources to manage the NADP/NTN Quality Assurance Program on a topical basis.

Collocated station comparisons between NADP/NTN and other networks as well as between side-by-side equipment within the NADP/NTN network are still woefully lacking even though

NADP/NTN has become the reference for deposition monitoring in North America. Collocated equipment is beginning to appear around the network, however, the interpretation of the information gathered through these studies is not being analyzed for the benefit of the NADP/NTN monitoring program and in some cases not at all.

- A quality assurance program specifically designed to estimate network precision and bias should be developed and implemented as soon as possible. Emphasis should be placed on comparisons within NADP/NTN and between peer network *data* rather than between the networks' protocols (e.g. daily vs weekly sampling, laboratory A vs laboratory B, etc.)
- The comparability of NADP/NTN data to that of other major networks operating in North America should be expanded.

SECTION 4
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SECTION 5

Procedures for Determining Analytical Method Comparability at the Central Analytical Laboratory (CAL)

Network Operations Subcommittee
National Atmospheric Deposition Program
AdHOC Committee on Analytical Method Comparability
October 1989

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Procedures for Determining Analytical Method Comparability At The Central Analytical Laboratory (CAL)

Network Operations Subcommittee, National Atmospheric Deposition Program
AdHOC Committee on Analytical Method Comparability, October 1989

Introduction

One of the many responsibilities of the Network Operations Subcommittee (NOS) is to advise the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) Technical Committee on issues relating to the Central Analytical Laboratory (CAL). The NOS evaluates the current analytical methods used by the CAL based on a variety of quality assurance and quality control data obtained from periodic reviews of the CAL, the Interlaboratory Comparison Program, and the annual report *Quality Assurance Report, NADP/NTN Deposition Monitoring: Laboratory Operations* prepared by the CAL. The NOS assumes that advances in analytical chemistry will produce both techniques and methods that will enhance the CAL's ability to analyze atmospheric deposition and encourages the implementation of improved, validated methods. In order to evaluate new, improved analytical methods that will be the standard operating procedures of the CAL, the NOS requires that the CAL follow a work plan that generates a prescribed data set that is submitted to the NOS. The NOS will evaluate this data set and make recommendations to the NADP Technical Committee which either approve or disallow the analytical chemistry method change or, describe additional data required to complete the method evaluation. A report describing the comparability and the quality assurance and quality control data of both methods will be reported in the appropriate CAL quality assurance report.

A. CAL Method Validation Protocol

The NOS expects the CAL to investigate the normal elements of an analytical method. The elements should include:

(1) Analytical range

(2) Method detection limit

(3) Potential Interferences

(4) Precision

(5) Analyte recovery (Bias)

(6) Carry-over, that is high concentration samples influencing the analysis of subsequent low concentration samples.

(7) Detailed summary of the proposed method, including a comparison of data produced by the validation testing (section C).

After the proposed method has been developed by the CAL, the CAL will produce a summary for NOS to examine.

Sample and Data Set Description

One data set will represent results obtained using the current standard methodology. The second data set will represent results obtained using the proposed methodology. Each of the two data sets will consist of the following sample results:

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a) At least 10 replicates of each calibration standard.

b) At least 10 replicates of one precipitation reference material that is of a different material than in a).

c) At least 10 replicates of 2 spiked natural samples that emulate the 50th and 75th percentile concentrations of NADPNTN precipitation samples of the previous year.

d) Ten natural precipitation samples whose concentrations are in the lower quartile of concentrations found in the previous year's precipitation.

e) Ten natural precipitation samples whose concentrations are in the upper quartile of concentrations found in the previous year's precipitation.

f) Ten natural precipitation samples whose concentrations are between the 25th and 75th percentile concentrations found in the previous year's precipitation.

g) Twenty additional natural precipitation samples selected randomly.

The total number of samples analyzed will include 60 different solutions assuming 5-7 calibration standards are used in a).

B. Equal-Variance Testing

(1) Determine the variance of both the approved and proposed method. The variance is calculated from a minimum of 10 replicate determinations on 2 different days by both the approved and proposed method of each calibration standard, one precipitation reference material, and 2 spiked natural samples. The natural samples are to be spiked with the analyte of interest to emulate the 50th and 75th percentile concentrations of precipitation collected by the NADP/NTN.

(2)

a. Test the differences between the approved and proposed method results obtained in B(1) for the assumption of normality. State the test used and summarize the results of the test.

b. Calculate a pooled mean and standard deviation for the replicate determinations separately for each data set. Within each data set, pool the calibration standards and reference material separately from the spiked natural samples. Then pool all data by each method and report the overall pooled mean and standard deviation of each method. Present these data in a table within the Analytical Method Comparison Report.

c. Test the data from B(1) for the equal-variance assumption. The test used must be appropriate based on the results from section B(2)a. for normality. If the data are determined to be non-parametric, a ranking technique is to be used to determine the equal-variance assumption. Name the test used to determine equal-variance and state the results and conclusion in the Analytical Method Comparison Report.

d. If the assumption of equal variance is rejected but the variance of the approved method is larger than the proposed method, proceed to the validation testing (section C).

e. If the assumption of equal variance is rejected and the variance of the proposed method is larger than the approved method, it is suggested the source of

variance be investigated before proceeding to the validation testing.

f. If variances are equal, proceed to Validation Testing (section C).

C. Validation Testing

(1) Select a minimum of 50 natural precipitation samples that were received by the CAL within the previous 3 months. Thirty of the fifty samples must be selected so that the distribution is as follows:

a. 10 samples whose concentrations are among the less than 26% of last year's NADP/NTN concentration distribution;

b. 10 samples whose concentrations are among the greater than 75% of last year's NADP/NTN concentration distribution;

c. 10 samples whose concentrations are among the 25-75% concentration distribution.

(2) Analyze each sample by the approved and proposed methods.

(3) Spike all samples whose results are less than the detection limit of the approved method to obtain concentrations not to exceed 5 times the method detection limit. The natural sample is to be spiked with the analyte of interest and then split to prepare duplicate samples.

(4) Analyze each spiked sample by the approved and proposed methods.

(5) Combine the spiked sample data set with the detectable-concentration data set and compare the approved and proposed data sets using a paired t-test (Dixon and Massey, 1969) at the 95% confidence interval.

(6) Compare the measured t statistic to the table *t* statistic.

(7) If the hypothesis that the two data sets are the same is rejected, calculate a regression equation that equates the proposed method results to the approved method results.

(8) Wait a minimum of one week and repeat steps C(1) through C(7) following the same protocol.

D Reporting to the Network Operations Subcommittee

(1) Prepare a report using tables that compare the following from each method:

a. Analytical range - state the range tested and range to be used for NADP/NTN samples.

b. Method detection limit - state the method used to calculate the limit and compare it to the approved method's detection limit. Also compare the proposed method's detection limit to the reporting limits used in current NADP/NTN data reports.

c. Potential Interferences (both chemical and physical) - state only those that are appropriate for atmospheric deposition samples.

d. Precision - Report the results from the equal-variance test [section B(1)].

e. Analyte recovery (bias) - in percent, obtained from the initial proposed-method evaluation by the CAL. State the range tested, mean and standard deviation, and state if the recovery appears to be concentration dependent.

f. Measured t statistic from both paired t-tests - State the hypothesis and results of t-tests.

g. Results of 'carry-over' testing, obtained from the initial proposed method evaluation by the CAL. The number of cases studied and frequency of carry-over problems.

h. Regression analysis - prepare regression equations for each repetition of the 50 natural samples in B(1). Then combine each repetition into a single data set and repeat the regressions analysis. Examine the residuals produced by the regressions analysis for goodiness of fit and state the coefficient of determination (R^2).

(2) Prepare a table listing the concentration data from both methods for both sets of natural samples.

(3) Prepare a recommendation for the NOS including any probable effects on NADP/NTN data.

E. Approval of Proposed Method by Network Operations Subcommittee

(1) The CAL will send a copy of the report comparing the accepted and proposed method to the NOS chair.

(2) The NOS chair will check the report to determine if all components of the Analytical Method Comparability Procedure have been addressed and notify CAL of the determination.

(3) The NOS chair will form an AdHOC committee to evaluate the report from the CAL and report to the Subcommittee at a scheduled meeting. The AdHOC committee will consist of one representative from the CAL and the USGS, the NADP/NTN Quality Assurance Manager and others appointed by the chair.

(4) A CAL representative will be present at the scheduled meeting to respond to inquiries of NOS.

(5) The NOS will make recommendations to the NADP Technical Committee as to the acceptance of the proposed new method.

SECTION 6

The Integration of Monitoring Data from a Second Laboratory into the NADP/NTN Data System

David S. Bigelow
Natural Resource Ecology Laboratory
Colorado State University
September 1989

The Integration of Monitoring Data from a Second Analytical Laboratory Into The NADP/NTN Data System

David S. Bigelow
NADP/NTN Quality Assurance Manager
Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO. 80523
September 1989

Introduction

Up until March of 1987, the NADP/NTN monitoring program used a single central analytical laboratory for the analyses of all of the samples collected during the previous nine years of the network's existence. In addition to the chemical analysis of collected samples, the laboratory, through its site liaison and data quality assurance activities, performed the most important network task of initially classifying field site and chemical analysis data quality.

Between March and September of 1987, 18 National Park Service (NPS) sponsored NADP/NTN monitoring sites utilized an alternate laboratory. The sites resumed using the previous central laboratory in October of 1987. Because of concerns about data comparability expressed by many of the NADP/NTN data users and program participants, and the strong desire to maintain the high level of standardization and data quality for which the program has come to be noted, data produced by the second laboratory was subjected to extensive and somewhat extraordinary scrutiny.

Based upon this report the network has concluded that field data from the second laboratory can and will be reported as is data from the central laboratory with no special caveats other than a code which indicates that the data is from an alternate laboratory. The large uncertainties in the chemical analysis results, however, preclude any distribution or publication of these data for network purposes. Un-edited original data will be maintained by the network for researchers requiring more highly or differently qualified data from these sites for the sampling periods affected.

This report describes the results of the data quality evaluations that were performed on the field and laboratory data reported by the second laboratory. For convenience the report divides its discussion into separate sections describing the comparability of field and laboratory data coding, the comparability of chemical analysis results and the overall conclusions and recommendations.

Comparability of Field and Laboratory Data Coding

Illinois State Water Survey (ISWS) personnel responsible for the site liaison and data quality coding activities at the NADP/NTN Central Analytical Laboratory (CAL) were asked to re-evaluate all of the Field Observer Report Forms (FORFs) and associated available information from the 18 National Park Service monitoring sites whose samples were analyzed by the second-laboratory between March and September of 1987. The Water Survey was asked to make this evaluation using the same procedures the CAL uses to evaluate typical NADP/NTN field data. This evaluation was done for two reasons. First, an initial review of the second-laboratory's data by the NADP/NTN Coordination Office, revealed that 'spsl style' coding (Bowersox, 1985) was applied more vigorously than had been done previously by the central

laboratory, but, only to the point of identifying the first reason for sample invalidation. Further checks for data invalidation did not appear to have been made or at least coded. It was felt that these omissions and others involving the coding and reporting of daily and weekly precipitation values would require the recoding of ALL of the second-laboratory's data. Secondly, since data coding at the second-laboratory had never been formally reviewed (data quality coding programs were not in place at the time of the two second-laboratory audits) and there was -and it appeared there would continue to be- doubts as to the comparability of the coding process, it was concluded that only ISWS re-coding would allow the data to be integrated into the NADP/NTN data system.

CAL data quality checks were applied to the data with the understanding that certain questions about the data might have to be answered by second-laboratory personnel before the checks could be completed. Some of the questions could not be resolved due to differences in procedures or a lack of available documentation. In these instances, assumptions were made and opinions rendered as to the most probable impact a negative response would have on the data. The important issues and questions raised during this re-evaluation and re-coding are listed below along with their final resolution.

- *The date samples were filtered at the second-laboratory is unknown. This is the only estimate of how soon after collection a sample has been analyzed.*

  The annotated date at the top of the FORFs is the date the sample was received at the second-laboratory. It is not guaranteed to be the date the sample was filtered or the date pH and conductance was determined. Generally, samples were filtered the same day they arrived at the laboratory, however, the protocols followed by the second-laboratory allowed up to four days after samples arrived before filtration was required. Since the documentation of the specific dates of analysis have only recently begun to be maintained in network documentation, they will not be used to determine data comparability. Network records will show these analysis dates to be missing.

- *Comments documenting laboratory observed sample contamination seem to be lacking except in a few instances. Perhaps the second-laboratory was not as effective in identifying or coding contaminated samples as the CAL.*

  Annotation added by the second-laboratory to the bottom of the FORF in the REMARKS block are the second-laboratory's comments. These laboratory comments address both contamination and the results of more than twenty observations (See Attachment 1) that relate directly to the assignment of 'spsl' coding. If contamination was not noted, it can be assumed that the person observing the sample as it arrived did not consider the sample to be contaminated beyond that already noted on the form. A lack of coding therefore, should be considered to be equivalent to CALs 'NON' coding which indicates explicitly, rather than implicitly, that contamination was not observed at the laboratory. While it was noted that CAL laboratory comments appear on virtually every field form but only a few appear on the second-laboratory's evaluated FORFs, it was also noted that the second-laboratory coded more samples as violating field protocols than did the CAL. Because of this it is assumed that other information on the FORF supports many of the conclusions that are additionally supported by CAL type laboratory comments and that the differences in the coding that might arise because of this 'difference in the way contamination is detected' are not significant.

The re-coding of the field data from the 18 sites serviced by the second-laboratory appears to have eliminated virtually all of the differences that might have arisen because of the differences in the interpretation of NADP/NTN coding procedures. It can be assumed that the quality of field data from these 18 NPS sponsored monitoring sites is completely compatible with other NADP/NTN field data and that it will require no special treatment or coding in the NADP/NTN data system.

Differences that may be noted in the completeness of the data records at NPS sites for 1987 as compared to previous years, however, is likely the unfortunate result of the process of switching to an alternate laboratory. It does not, however, reflect upon the second-laboratory's ability to perform the coding function.

Comparability of Chemical Analysis Results

The comparability of the chemical analysis results from one laboratory to another can be a straight-forward process if certain pre-planning has taken place. The NADP/NTN network did in fact review the types and frequency of data that would be available to make this type of laboratory comparison. Unfortunately, the conclusions derived from this review and the action taken were based upon the establishment of a long-term relationship with a second laboratory. The six months of quality assurance information that is available may not satisfy all users of this data. None-the-less, it is the only information that will be available. Once again, the important issues and questions raised during the comparability evaluation are identified below along with their final resolution.

It should be noted that a part of the re-coding request made to the Illinois State Water Survey was to subject the second-laboratory's chemical analysis results to the same outlier and re-analysis tests that are used for all other NADP/NTN precipitation chemistry samples. The Water Survey was asked to report the results of these and the previously mentioned FORF evaluations in the standardized manner that is used to report all other NADP/NTN data to the Coordination Office. Some of the questions raised in this section were specific to this process.

- *The CAL internally uses a weight taken after the sample arrives as the basis for computing dilution factors and for calculating adjusted, analyzed, concentration results. Since this information was not required of the second-laboratory by the NADP/NTN monitoring program, the Water Survey requested confirmation that dilution factors for 'WA' samples have already been applied to the reported data. This confirmation was necessary to ensure that their data quality tests would be meaningful.*

  The explicit dilution factors used by the second laboratory for 'WA' samples are given in Attachment 2. The CAL, however, did not need to correct 'WA' data for dilutions factors since the second-laboratory's staff had on numerous occasions, assured the Coordination Office that this correction had been made in all data sent to the Coordination Office and to the monitoring sites.

  An examination of the 'WA' data distributions of the second-laboratory's data as compared to previously reported NPS 'WA' data from the same seasonal time periods support this assertion, with the possible exception of the $PO_4^{=}$. Phosphate data from 'WA' samples have values at or near 0 in half of the reported values. If we assume that dilution factors for 'WA' samples are approximately 2-6, detected values would range from 0.0005 down to $0 \div 6$.

The fact that these 'WA' phosphate values and some values from other analytes appear to be derived from a calibration technique that accommodates very small numbers, or, as discussed next, negative numbers, only points out differences in data handling at the two laboratories. At the CAL, values below the method detection limit (MDL) are reported as censored numbers. The second-laboratory reported all values, letting the data user determine the level at which he believes censoring should take place. (See Environmental Science and Technology feature article [Vol. 22. No. 8, p856-861] titled *The detection limit* for a discussion of the merits of this approach).

- *The second-laboratory did not report detection limits on any of the final data reported to the Coordination Office. Values at and near zero, and below zero, are found in the data set. Since the NADP/NTN monitoring program defines its MDLs as 3 times the standard deviation of repetitive measurements made at or near the blank level* (Lockard, 1987), *the network must declare its own MDLs for the second-laboratory's data set.*

As mentioned previously, the reporting of zero and negative numbers represents an alternative way of presenting below MDL values to the data user. MDLs for this style of reporting can be derived from either information supplied by the second-laboratory, or, information gleaned from the external audit programs the second-laboratory participated in during the time period it served the NPS-NADP/NTN monitoring stations.

The second-laboratory was not able to provide the network with blank values (false positive indications) which would allow the computation of comparable MDLs. However, it was able to provide the network with two estimates of detection limits, preliminary printout estimates and 10% BPL estimates. Though neither of the estimates match the MDL definition used by the NADP/NTN central analytical laboratory, both are useful for comparisons to estimates derived from external quality assurance programs. The two estimates are explained below and listed in Table 1. A third estimate derived from a report on work done by the second-laboratory for another monitoring program (UAPSP, 1989) is also furnished in Table 1.

The second-laboratory participated in two USGS external quality assurance programs (See et al., 1989a and 1989b) during the time period of interest. In one of the programs, the Blind-Audit Program, directly shipped bottle analysis results have been lost by the second laboratory and cannot be recovered. The remaining bucket portion of the program is not appropriate to evaluate detection limits. The second program, the Interlaboratory Program, has only limited false positive results. However, because results from this program are reported on the same basis as are the second-laboratory's results for natural samples, detection limits can be calculated. MDLs calculated from blanks and low concentration reference samples submitted as a part of the Interlaboratory Program are included in Table 1. Values listed are derived from all Interlaboratory Program data produced by the second-laboratory in 1987. As a final reference, Table 1 lists the MDLs reported by CAL in 1987.

Explanation of the derivation of estimated detection limits used in Table 1.

Preliminary Printout - data sent to each field site under the conditions of its contract with the NPS, had detection limit values reported. The limits used for these reports were 3 times the standard deviation of values that were 5 times the blank levels.

10% BPL - (Below Precision Level) is a value that represents the concentration level where the relative pooled standard error of repeated measurements is approximately 10%. These values are based upon chemical analyses performed during the period of record the second-laboratory served as the primary laboratory for another monitoring network. The second-laboratory used the same chemical analysis techniques for both the NADP/NTN and other monitoring program.

UAPSP 117 - reports and defines the detection limits of the UAPSP program as 3 time the standard deviation of the reagent or calibration blank.

USGS blanks - computes detection limits as 3 times the standard deviation of the unknown, blank values submitted to the second-laboratory as a part of the USGS Interlaboratory Program.

USGS standards - computes detection limits as 3 times the standard deviation of the unknown, near-blank, NBS standard submitted to the second-laboratory as a part of the USGS Interlaboratory Program.

1987 CAL - reported detection limits of the CAL for 1987 (James, 1989).

Table 1 Suggested MDLs For data From The Second NADP/NTN Laboratory

	Preliminary	10%	UAPSP	USGS InterLab		1987
Element	Printouts	BPL	117	blanks	Standards	CAL
Ca^{++}	0.025	0.05	0.01	**0.018**	0.015	0.009
Mg^{++}	0.010	0.003	0.001	**0.003**	**	0.003
Na^{+}	0.025	0.04	0.001	**0.039**	**	0.003
K^{+}	0.025	0.05	0.002	**0.030**	**	0.003
NH_4^{+}	0.010	0.05	0.002	**0.015**	0.036	0.02
NO_3^{-}	0.005	0.04	0.004	**0.117**	0.015	0.03
$SO_4^{=}$	0.050	0.075	0.006	**0.072**	**	0.03
Cl^{-}	0.010	0.015	0.004	**0.045**	**	0.03
$PO_4^{\equiv}$	0.002	**	0.002	**	**	0.02
n	unknown	unknown	10	**13**	6-9	unknown

where ** indicates an estimate was not made

Based upon the examination of the available data the USGS blank-derived MDLs were chosen as the most comparable and reliable reporting limits for the second-laboratory determined NADP/NTN data. It is recognized that many of the chosen values and espetory. Because of this and to prevent a re-occurrence of the problems previously encountered in the use of network $PO_4^{=}$ data using ½ of the MDL in data summaries, it is recommended that values below the MDL be reported as missing rather than below the detection limit on both data reports and tapes. This action affects approximately 40 samples from 8 sites (primarily 3 sites).

cially the NO_3^{-} MDL are much higher than those listed for the central NADP/NTN labora-

Because of the brief period of second-laboratory participation in NADP/NTN monitoring activities, no formal quality assurance reports of the second-laboratory's operations were produced and no SRM performance results, sample replication-reanalysis results or false positive frequencies and levels were reported to the Coordination Office. What information is available for determining the comparability of precision and bias between the second-laboratory and the central NADP/NTN laboratory?

Neither results or summaries of results of re-analysis and sample replications are available from the second-laboratory for the specific time period that NPS-NADP/NTN samples were processed. The second-laboratory was able to furnish the network with two analyses of certified standard reference materials and with results of spiked blank recoveries reported to have been made during the period in which NPS samples were analyzed. For the SRMs, one analysis was of an NBS simulated precipitation sample (U.S. Department of Commerce, 1989) submitted to the second-laboratory as a part of its own external quality assurance program and the other was a series of 10 solutions measured as a result of its participation in the L-16 LRTAP Interlaboratory Comparability Study (Aspila, 1987). By coincidence, the NBS SRM was also analyzed as an unknown sample in the USGS Interlaboratory Program. Results of NBS reference sample analyses from both quality assurance programs are shown in table 2.

Table 2 NBS SRM Results

Element	In-house External QA	USGS Interlaboratory Program *	NBS Certified Values
Ca^{++}	0.00†	0.007†	0.014†
Mg^{++}	0.023	0.024	0.024
Na^{+}	0.200	0.201	0.205
K^{+}	0.045	0.052	0.052
NH_4^{+}	0.012†	0.003†	*
NO_3^{-}	0.168	0.175	‡
$SO_4^{=}$	2.61	2.51	2.75
Cl^{-}	0.265	0.267	(0.24)
$PO_4^{=}$	‡	‡	‡
pH	4.26	4.29	4.27
Conductance	25.	25.7	26.0

* mean of 9 replicates measured on different days throughout 1987.
† below calculated detection limit
‡ not Certified

For certified analyses that are above the computed, USGS based detection limits (table 1), there appears to be no bias except for $SO_4^{=}$. Analyses of this SRM does not, however, support the LRTAP findings for $SO_4^{=}$ or Mg^{++}.

LRTAP results indicate no bias for analyses of Ca^{++}, Na^{+}, K^{+}, $NO_3^{=}$, $SO_4^{=}$, Cl^{-}, pH and conductance although pH results identified as being from precipitation samples were noted to be biased low (not very low). Mg^{++} was biased high, and, NH_4^{+} and $PO_4^{=}$ were not determined.

Results of the analysis of the NBS SRM indicate that Mg^{++} does not show a bias while LRTAP did, and, that $SO_4^{=}$ does show a bias while the LRTAP study did not. The reason for the discrepancy in the Mg^{++} results are not known. $SO_4^{=}$ discrepancies will be discussed later in this report.

Deionized water results from the USGS Interlaboratory Program were summarized in table 1, and table 2 included a summary of the simulated rain sample results. Table 3 offers a more direct comparison of the second-laboratory's chemical analysis results to those of the central NADP/NTN laboratory using 1987 natural sample and simulated rain sample results from the USGS interlaboratory comparison. Because both laboratories participated in the USGS program during 1987, their results may be compared directly using a *t* test. A rank test (reference) is used to make the comparison since the laboratories reported an unequal number of samples.

Results of this direct comparison indicate significant differences at $t_{.95}$ for sodium and potassium for natural samples only. This is not surprising considering that 45% of the sodium values and 55% of the potassium values from the second-laboratory are below the MDLs in table 1 but above the CAL MDL. For Mg^{++} and $SO_4^{=}$, the analytes displaying bias in table 2 or in the LRTAP study, there were no significant differences. These results are consistent with the small positive bias for Mg^{++} reported by the CAL in its 1987 quality assurance report (James, 1989) but not consistent with the positive bias reported for $SO_4^{=}$.

Table 3 Direct Comparison of the Second and Central NADP/NTN Laboratories

Element	Natural Samples			Simulated Rain		
	df	*t* prob.	Median/ QRTdev	df	*t* prob.	Median/ QRTdev
Ca^{++}	95	0.451	0.061/ 0.045	70	0.611	0.305/ 0.209
Mg^{++}	95	0.650	0.017/ 0.010	70	0.907	0.076/ 0.087
Na^{+}	95	**0.968**	0.048/ 0.061	70	0.249	0.133/ 0.127
K^{+}	95	**0.948**	0.022/ 0.022	70	0.536	0.103/ 0.096
NH_4^{+}	95	0.496	0.165/ 0.107	56	0.016	-0.018/ 0.042
NO_3^{-}	94	0.466	0.706/ 0.304	71	0.758	0.299/ 0.332
$SO_4^{=}$	94	0.634	1.083/ 0.512	71	0.303	2.277/ 0.603
Cl^{-}	94	0.658	0.095/ 0.067	71	0.714	0.299/ 0.236
$PO_4^{\equiv}$	95	*	*	71	*	*
pH	95	0.687	4.86 / 0.334	71	0.874	4.42 / 0.167
Conductance	95	0.323	11.00/ 4.40	71	0.710	21.00/ 5.85

where df is the degrees of freedom of the test; t prob is the significant level of the test; and Median/ QRTdev is the median of sample means along with the quartile deviation of the distribution of the means.

The second-laboratory additionally furnished the NADP/NTN Coordination Office with quality control summaries of spiked blank recoveries for what is reported to be the period during which NPS samples were analyzed (See the discussion concerning sulfate below). Table 4 summarizes the results and analysis dates by element.

Table 4 Summary of Spiked Blank Results (QCCS) From The Second-Laboratory

Element	n	Mean	SD	Levels (mg/L)	Analysis Dates
Ca^{++}	18	101.	2.59	0.5	02 Sep - 04 Nov 87
Mg^{++}	18	101.	3.08	0.1	02 Sep - 04 Nov 87
Na^{+}	18	99.8	1.77	0.5	02 Sep - 04 Nov 87
K^{+}	18	99.0	2.35	0.5	02 Sep - 04 Nov 87
NH_4^{+}	152	99.7	7.79	0.5, 2.5	17 Sep - 22 Apr 88
NO_3^{-}	93	100.	2.68	0.6, 4.0	03 Sep - 23 Dec 87
$SO_4^{=}$	121	99.2	3.20	0.6, 4.0	03 Sep - 21 Apr 88
Cl^{-}	108	100.	2.94	0.12, 0.8	03 Sep - 21 Mar 88
$PO_4^{=}$	121	101.	4.2	0.05, 0.25	17 Sep - 20 Apr 88
pH	25	101.	0.38	4.30, 6.00	01 Oct - 28 Sep 87
Conductance	19	100.	0.29	75.0	01 Oct - 28 Sep 87

The comparison summarized in table 3 and the results of the SRM analyses suggest that the second-laboratory, with the exception of detection limit reporting, performed with comparable quality as did the central NADP/NTN laboratory (the CAL). Sulfate analyses however, are somewhat inconclusive since SRM analyses indicates a possible negative bias for the second laboratory but a direct comparison to the CAL indicates no differences, even though the CAL reports a positive bias. Similar conclusions of laboratory comparability, at least for bias, may be inferred from the 1987 USGS NADP/NTN report of its external quality assurance programs (See et al., 1989a). Precision estimates given in this report, however, indicate that the second-laboratory's values are less precise than those of the CAL for NA^{+}, K^{+}, Cl^{-}, pH and Conductance for natural samples and for Ca^{++} for both natural and simulated samples. The higher detection limits that were estimated in table 1 further support this conclusion.

- *In reports to the second-laboratory's other monitoring network, the laboratory identifies a sulfate bias in samples analyzed between October 1987 and April of 1988. This time period coincides with the analysis dates given in table 4 for NPS-NADP/NTN samples. Are samples analyzed for the NPS-NADP/NTN monitoring sites similarly affected?*

  The $SO_4^{=}$ bias reported by the UAPSP monitoring program [See Attachment 3 (Topol, 1989)] for the period October 21, 1987 through March of 1988, concludes that values from samples whose pH is below 5.0 are unreliable and should not be used because of an uncorrectable negative bias. Both the low NBS SRM results (table 2) and the low LRTAP results have been attributable (by the second-laboratory staff) to this problem. These results are very curious however when one considers the results of the direct comparison between CAL and the second-laboratory (table 3). The direct comparison indicated no significant differences in $SO_4^{=}$ in spite of the fact that CAL reported a positive bias while the second-laboratory acknowledges a negative bias.

  In order to understand the discrepancies identified in the sulfate quality assurance results a number of possible explanations were identified and to the extent possible tested.

Possible explanations considered were:

(1) Quality assurance samples were given preferential treatment and are therefore not representative of the natural samples submitted through the NPS-NADP/NTN monitoring effort.

(2) The dates in table 4 are correct, but quality assurance results were not produced concurrently with unknown sample results.

(3) The second-laboratory analyzed all or part of the samples on dates other than those reported in table 4.

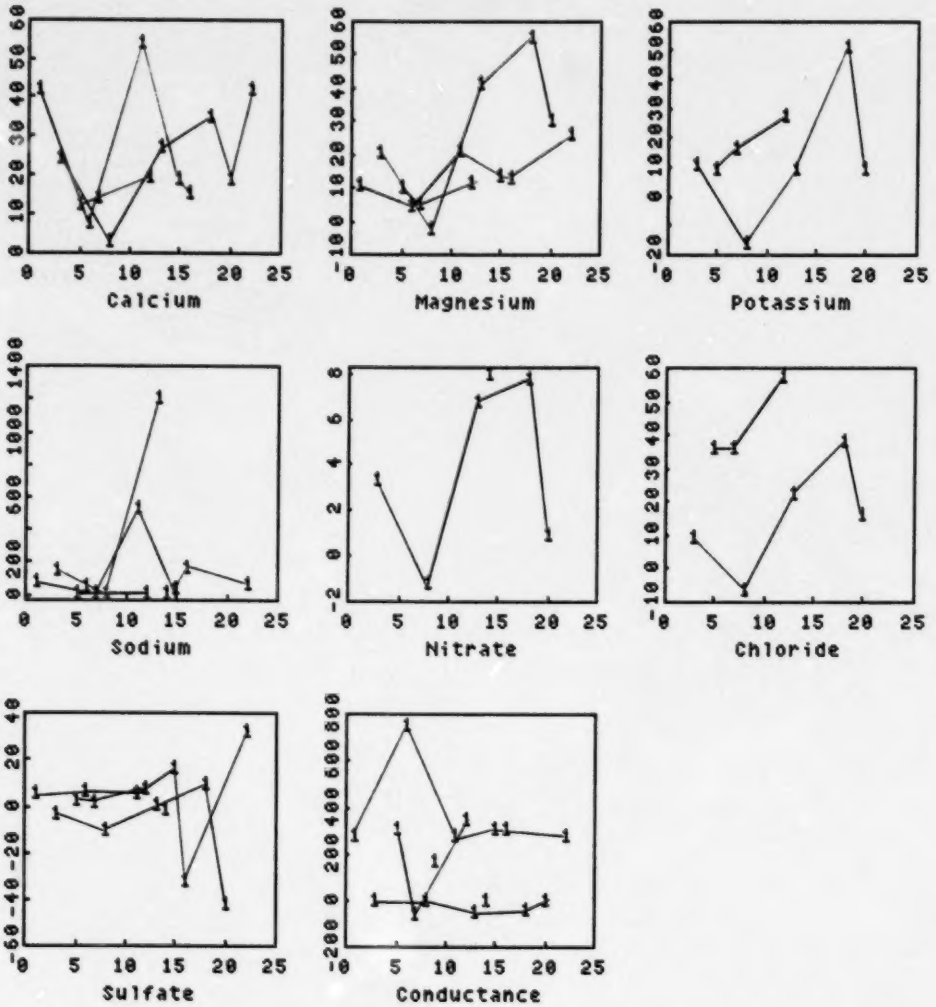
There is no evidence in data examined for this report that supports the first explanation above. Results presented in tables 1 and 2, in fact, suggest just the opposite, that is that quality assurance samples were not given preferential treatment. The second explanation is likewise not supported since some quality assurance results do reflect problems consistent with the reported sulfate bias.

Since the second-laboratory was not able to provide specific analysis dates for each sample the third explanation, the most plausible, could only be tested indirectly. This explanation is supported by the knowledge that the second-laboratory sent field sites and the NADP/NTN Coordination Office preliminary data prior to the earliest dates given in table 4. A comparison of the early data to the final data reveals that approximately 10% of the sulfate values changed, but the change was typically less than 1%. For other analytes up to one-third of the samples had changed. Though the number of changes in analytical data is more than an order-of-magnitude more than has been normal in the network preliminary data, it is consistent with a laboratory quality assurance sample replication regime. In the above comparison one-third of the atomic absorption values and 10% of the ion chromatography values were changed while 10% of the ammonium and 66% of the phosphate values were changed. The grouping of the number of replacements by instrument type and the small difference in the values suggests a re-analysis/replication protocol.

Further evidence for the third explanation comes from an examination of the USGS blind-audit data (See et al., 1989b). In the Blind-Audit Program samples are submitted to the laboratory, once per week through a field site. Since the samples are sent from a field site it follows the same analysis schedule as normal natural samples. Plotting the blind-audit results against time should reveal an anomaly during the time period when sulfate results are in question.

Figure 1 plots the percent bias observed in blind-audit samples analyzed by the second-laboratory ((laboratory value minus the expected value)/ expected value) for those values that are above the detection limits listed in table 1. Multiple lines on each graph represent different audit solution types. The week of analysis is given as the x-axis. Since the bottle portion of the Blind-Audit Program was not analyzed by the second-laboratory the plot cannot be used to estimate true laboratory bias. However, if you assume that the blind-audit samples do not deteriorate over time, they can be used to estimate overall bias due to sample handling, shipment AND laboratory analyses [see See et al., 1989a]). The *change* in bias however, can be used as an indication of when if at all, a sulfate problem did arise.

Figure 1. Percent Bias in Blind-Audit Program Results From The Second Laboratory



The $SO_4^=$ plot clearly shows some problem beginning in week 15. This corresponds to samples submitted to the laboratory in mid July, exactly the time period reported as suspect in the laboratory's report to its other monitoring network (Topol, 1989). The agreement in results between the second-laboratory and the CAL implied in table 3 is most likely the result of the poorer precision in the second-laboratory's data and the fact that approximately half of the quality control information was produced during a period where there was no analytical problem. If analysis dates for the quality assurance data were available this could most likely be confirmed.

Based upon the available information and the fact that the source of the bias has not been identified, NADP/NTN $SO_4^=$ results for samples with a date off after June 16, 1987 should be coded as missing. This allows for the one month lag in chemical analysis allowed by the second-laboratory's contract with the NPS.

- *There are approximately 8 samples that have recorded pH measurements that are inconsistent with their corresponding conductance values. Also approximately 17% of the samples have an ion imbalance. At the CAL these inconsistencies are resolved before data is finalized. How will this be resolved in the data from the second-laboratory?*

As mentioned previously, reanalysis/ replication results are not available to resolve these issues. For pH, two of the cases mentioned may be a result of the normal uncertainty in pH measurements (pH's above 5). The other cases however, appear to reflect poor pH or conductance values. Since re-analysis values are not available for these samples the values should be recorded as missing in the data set thereby forcing the data user to use either the field values or a calculated pH or conductance value based upon the other cation and anion analysis.

Ion imbalances are known to arise when there is an unmeasured analyte in a sample analysis, when laboratory contamination occurs during sample processing or when analytical measurements from one analyte inadvertently gets coded as another analyte during laboratory computations or data entry/ data management operations. Because of the long history with each of the NPS sites and the fact that the imbalances occur in samples from all of the sites across all sampling dates gives confidence that the problem is not due to a missing analyte. Laboratory contamination would seem the most likely cause considering the $SO_4^=$ and the problems with detection limits. However, if samples having these problems are eliminated from the ion balance evaluation, more than 20% of the remaining samples ($n = 83$) still exhibit ion imbalance. The magnitude of the imbalance (median = 27%) can only lead to the conclusion that the analytes have been mixed.

As with the inconsistent pH values, values displaying ion imbalance that cannot be attributable to contamination of any one or more specific analytes should be coded as missing to be consistent with NADP/NTN integrity considerations.

Conclusions and Recommendations

The evaluation of field and laboratory data processed and produced by the second-laboratory has resulted in the following conclusions and recommendations:

1) Field data processed by the second-laboratory and re-coded by the Illinois State Water Survey is directly comparable to similar previous information gathered by the NADP/NTN monitoring program. This information should be entered transparently into the NADP/NTN data base. A new notes code of 'L2' should be entered into the notes code field to alert data users that this information was partially processed by a second laboratory. This action is protection against some future data quality problem that might be identified by other users of this information.

2) Chemical analysis results from the second laboratory require higher reporting limits than values previously analyzed in the NADP/NTN monitoring program. In addition, though the results do not appear to be biased, the results do appear to be less precise and ion balances

are poorer for many more samples than has been typically observed in other network data. Finally, a sulfate bias problem prevents the use of approximately half of the sulfate data from NPS sites for this 26 week period.

These finding suggest that chemical analysis results from second laboratory are not consistent with other NADP/NTN analytical data and that their inclusion in the network data base would diminish from the high level of data integrity for which the network has come to be known. It is recommended that all chemical analysis results from the second laboratory be reported as missing and that the 'L2' notes code mentioned above carry the following explanation. *Data produced by a second laboratory, chemical analysis results are not considered to be comparable to other NADP/NTN chemical analysis data. Data is only available by special request.*

3) Original, CAL flagged, data from the second laboratory should be maintained separately in the NADP/NTN data base in its original form (negative detection limits, no sequestered values) for data users requiring a less rigorous data quality evaluation. A separate data structure will also allow for an easy re-interpretation of results should future data quality information become available that would address the deficiences mentioned in this report.

4) All data tapes, reports and special requests (including reports to the ADS data system) should not include the sequestered data from the second laboratory. NO further restriction on the use of the data should be imposed by the NADP/NTN monitoring program except that a copy of this report should accompany all requests for this data.

Acknowledgement

I would like to thank Mary Ann Allan and the Electric Power Research Institute for allowing those portions of UAPSP Draft Report no. 117 specific to the sulfate contamination problem to appear in this report.

I would also like to thank Tim Willoughby at the Quality Assurance Branch of the USGS National Water Quality Laboratory in Denver, CO for his help in summarizing and analyzing USGS-NADP/NTN external quality assurance data.

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Attachment 1 Contamination and Other Codes Used By The Second Laboratory to Screen and Assign SP/SL coding to NADP/NTN Monitoring Data

F Code Comments (for the SL box)

1. Lid not secured (leaking during shipment - bag is wet inside)
2. Sample Period > 16 Days
3. No Foam Seal on Collector
4. Samp Bucket Rinsed at Site
5. Field Chem Done in Bucket
6. Sample Shipment> 60 Days
7. Operator Contaminated Samp
8. Most Samp Spilled at Site
9. Nonstd Lid Used by Site
10. Nonstd Bucket Used by Site
11. All Samp Leaked in Shipment
12. Sampler & R Gage > 0.05" Diff
13. Insufficient Sample for Analysis (L code)

Leak _____ = N or Y and A, B or C

A is less than 10g. leaked out during shipment
B is greater than 10g. & less than or equal to 100g. leaked out
C is greater than 100g. of sample leaked out

U Code Comments (for the SP box)

1. Sampler Malfunc- Sensor (priority 2)
2. Sampler Malfunc- Motor (fuse) (priority 1)
3. Sampler Malfunc- Event Rec (evaporation) (priority 3)
4. Snow Overflow
5. Diff Lab & Field Samp Wt (noticed from box 7 of F.Form)
6. Multiple Non Rain Incident
7. Precip Rec From Noan Stn
8. Precip Rec From Unk Source

U (unknown, undefined) not sure if the bucket was covered during dry deposition for 6 hours or more, or you can see on R.chart that lid was open 6 or more hours during dry dep. (no rain)

Q (Blind Audits) in SP box (If you have evidence of a leak and bag is not wet and operator didn't write down that sample spilled, a small is assigned in SL box.)

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Attachment 2 Dilution Factors Used by The Second Laboratory to Adjust Volumes of NADP/NTN Samples Classified as Lab Type 'WA'

Dilution Factors to be written on Wet-Add (WA) samp

ml of Sample	Dilution Factor	ml of Sample	Dilution Factor	ml of Sample	Dilution Factor	ml of Sample	Dilution Factor	ml of Sample	Dilution Factor	ml of Sample	Dilution Factor	ml of Sample	Dilution Factor	ml of Sample	Dilution Factor
10.0	6.0	14.0	4.57	18.0	3.78	22.0	3.27	26.0	2.92	30.0	2.67	34.0	2.47	38.0	2.32
.1	5.95	.1	4.55	.1	3.76	.1	3.26	.1	2.92	.1	2.66	.1	2.46	.1	2.31
.2	5.90	.2	4.52	.2	3.75	.2	3.25	.2	2.91	.2	2.66	.2	2.46	.2	2.31
.3	5.85	.3	4.50	.3	3.73	.3	3.24	.3	2.90	.3	2.65	.3	2.46	.3	2.31
.4	5.81	.4	4.47	.4	3.72	.4	3.23	.4	2.89	.4	2.64	.4	2.45	.4	2.30
.5	5.76	.5	4.45	.5	3.70	.5	3.22	.5	2.89	.5	2.64	.5	2.45	.5	2.30
.6	5.72	.6	4.42	.6	3.69	.6	3.21	.6	2.88	.6	2.63	.6	2.45	.6	2.30
.7	5.67	.7	4.40	.7	3.67	.7	3.20	.7	2.87	.7	2.63	.7	2.44	.7	2.29
.8	5.63	.8	4.38	.8	3.66	.8	3.19	.8	2.87	.8	2.62	.8	2.44	.8	2.29
.9	5.59	.9	4.36	.9	3.65	.9	3.18	.9	2.86	.9	2.62	.9	2.43	.9	2.29
11.0	5.55	15.0	4.33	19.0	3.63	23.0	3.17	27.0	2.85	31.0	2.61	35.0	2.43	39.0	2.28
.1	5.50	.1	4.31	.1	3.62	.1	3.16	.1	2.85	.1	2.61	.1	2.42	.1	2.28
.2	5.46	.2	4.29	.2	3.60	.2	3.16	.2	2.84	.2	2.60	.2	2.42	.2	2.28
.3	5.42	.3	4.27	.3	3.59	.3	3.15	.3	2.83	.3	2.60	.3	2.42	.3	2.27
.4	5.39	.4	4.25	.4	3.58	.4	3.14	.4	2.82	.4	2.59	.4	2.41	.4	2.27
.5	5.35	.5	4.23	.5	3.56	.5	3.13	.5	2.82	.5	2.59	.5	2.41	.5	2.27
.6	5.31	.6	4.21	.6	3.55	.6	3.12	.6	2.81	.6	2.58	.6	2.40	.6	2.26
.7	5.27	.7	4.18	.7	3.54	.7	3.11	.7	2.81	.7	2.58	.7	2.40	.7	2.26
.8	5.24	.8	4.16	.8	3.53	.8	3.10	.8	2.80	.8	2.57	.8	2.40	.8	2.26
.9	5.20	.9	4.14	.9	3.51	.9	3.09	.9	2.79	.9	2.57	.9	2.39	.9	2.25
12.0	5.17	16.0	4.13	20.0	3.50	24.0	3.08	28.0	2.79	32.0	2.56	36.0	2.39	40.0	2.25
.1	5.13	.1	4.11	.1	3.49	.1	3.07	.1	2.78	.1	2.56	.1	2.39		
.2	5.10	.2	4.09	.2	3.48	.2	3.07	.2	2.77	.2	2.55	.2	2.38		
.3	5.07	.3	4.07	.3	3.46	.3	3.06	.3	2.77	.3	2.55	.3	2.38		
.4	5.03	.4	4.05	.4	3.45	.4	3.05	.4	2.76	.4	2.54	.4	2.37		
.5	5.00	.5	4.03	.5	3.44	.5	3.04	.5	2.75	.5	2.54	.5	2.37		
.6	4.97	.6	4.01	.6	3.43	.6	3.03	.6	2.75	.6	2.53	.6	2.37		
.7	4.94	.7	3.99	.7	3.42	.7	3.02	.7	2.74	.7	2.53	.7	2.36		
.8	4.91	.8	3.98	.8	3.40	.8	3.02	.8	2.74	.8	2.52	.8	2.36		
.9	4.88	.9	3.96	.9	3.39	.9	3.01	.9	2.73	.9	2.52	.9	2.36		
13.0	4.85	17.0	3.94	21.0	3.38	25.0	3.00	29.0	2.72	33.0	2.52	37.0	2.35		
.1	4.82	.1	3.92	.1	3.37	.1	2.99	.1	2.72	.1	2.51	.1	2.35		
.2	4.79	.2	3.91	.2	3.36	.2	2.98	.2	2.71	.2	2.51	.2	2.34		
.3	4.76	.3	3.89	.3	3.35	.3	2.98	.3	2.71	.3	2.50	.3	2.34		
.4	4.73	.4	3.87	.4	3.34	.4	2.97	.4	2.70	.4	2.50	.4	2.34		
.5	4.70	.5	3.86	.5	3.33	.5	2.96	.5	2.69	.5	2.49	.5	2.33		
.6	4.68	.6	3.84	.6	3.31	.6	2.95	.6	2.69	.6	2.49	.6	2.33		
.7	4.65	.7	3.82	.7	3.30	.7	2.95	.7	2.68	.7	2.48	.7	2.33		
.8	4.62	.8	3.81	.8	3.29	.8	2.94	.8	2.68	.8	2.48	.8	2.32		
.9	4.60	.9	3.79	.9	3.28	.9	2.93	.9	2.67	.9	2.47	.9	2.32		

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Attachment 3 Excerpts from UAPSP Draft Report 117 Explaining the $SO_4^=$ Bias

UAPSP NETWORK DESCRIPTION

AND MEASUREMENTS FOR 1981 THROUGH 1987

UAPSP 117

1 MARCH 1989

Prepared by

ENVIRONMENTAL MONITORING AND SERVICES INC.
4765 Calle Quetzal
Camarillo, California 93010

Principal Investigator
L. E. Topol

Prepared for
Utility Acid Precipitation Study Program

and

Electric Power Research Institute
3412 Hillview Avenue
Palo Alto, California 94304

EPRI Project Managers
P.K. Mueller
M.A. Allan

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Inaccuracy in Sulfate Measurements in Late 1987. Audit samples of pH below 5.0, analyzed at the end of October until the end of the program, yielded low sulfate values. No cause for the malfunction of the ion chromatograph could be determined. The problem was corrected near the end of the program by replacing the ion exchange and fiber suppressor columns of the ion chromatograph.

The audit sample data could be corrected by the relation, $\Delta SO_4 = 9.9(H^+)$, where ΔSO_4 is the error in SO_4 in mg/l and (H^+) is the hydrogen ion concentration of the sample in mg/l. To determine if this relation served as an acceptable means of adjusting the precipitation sulfate, charge balance results were used as the test. An examination of monthly charge balance data showed that a large deficit in anions occurred initially for samples collected in August 1987, and persisted through the end of the year. With daily charge balance data, the malfunction was determined to have begun on analysis days, October 26th and 27th, 1987. The precipitation sulfate data for samples analyzed after October 26, 1987 were then adjusted using the above relation. It was found that the values analyzed early after the October 26th date were overcorrected, while later samples were undercorrected. Thus, the sulfate data for samples collected in late July through December 1987 are low and should be used with extreme caution.

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Inaccuracy in the Sulfate Measurements in 1987

There appears to have been a malfunction of the ion chromatograph towards the end of 1987. As a result, the accuracy of the sulfate measurements performed during this period cannot be guaranteed; nitrate and chloride measurements made by the same instrument appear not to have been affected. The malfunction was not detected by routine quality control procedures; the recovery of all quality control check standards remained within specifications, and repeat measurements of split rainwater samples showed only minor variations from day to day. A brief chronology of the malfunction follows.

October 1987. The RTI external audit in October, 1987, showed one low result (10.1%) for sulfate. Though a majority of the results were still within specifications, the auditor suspected that there might be a malfunction.

January 1988. The Canadian LRTAP 17 audit showed that for three of ten samples the sulfate readings were low and outside specifications. Later examination showed that these three samples all had a pH less than 5.

March 1988. The RTI auditor submitted five sulfate samples. For three of these, sulfate was within specifications; these solutions were of pH approximately 7. For the other two samples, both of pH less than 5, the readings were very low, far outside specifications.

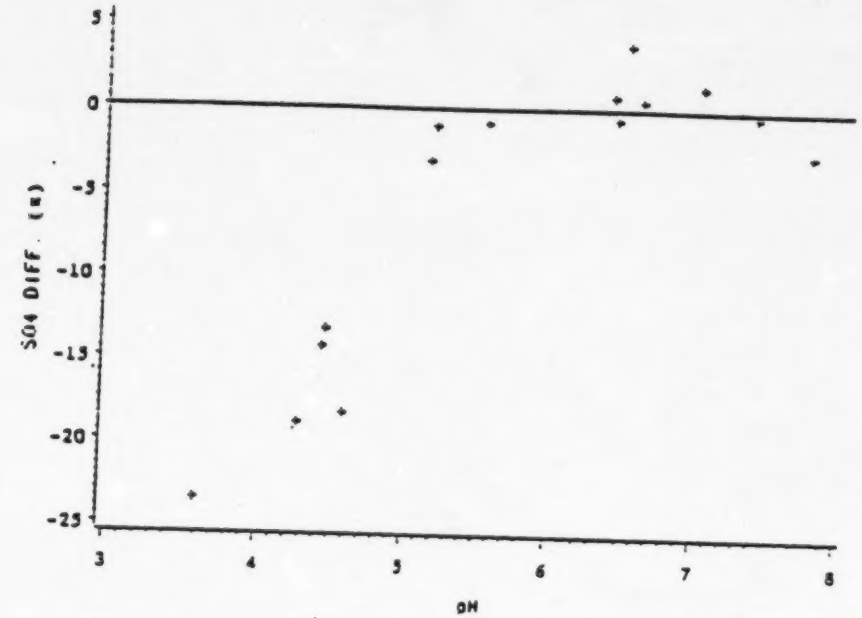
April 1988. Routine service of the ion chromatograph was made. The fiber suppressor and ion exchange columns were replaced, and the former was found to be "green and gunky". There were no problems with sulfate analysis after this date.

October 1988. Re-analysis of OEN rainwater samples first measured in March 1988 showed the March results to have been low and outside specifications both for acidic samples, pH < 5, and for almost neutral samples, pH ≈ 6.5.

The data from the LRTAP-17, NBS, and RTI samples, analyzed in January and March, 1988 are given in Figure 6-41a. The percent difference, given by 100 (measured SO_4 - designated SO_4)/designated SO_4, show an apparent pH effect with the sulfate error appearing below pH = 5 and increasing with decreasing pH.

To gather additional evidence of the effect of pH on sulfate analysis, the laboratory in October 1988, when the sulfate problem no longer existed, reanalyzed precipitation samples which had been originally analyzed in the last two weeks of March during the time of the sulfate problem. The samples reanalyzed were from EPRI's "Operational Evaluation Network" (OEN) and covered the pH range 4.31 to 6.54. The samples had been stored at 4°C and it was assumed that negligible degradation of the sulfate has occurred. These sulfate results, plotted as (March values - October values)/October values, are presented in Figure 6-41b and also show that the sulfate results in March were low for pH below 5.1; however, for pH greater than 5.1, the differences,

(a)



(b)

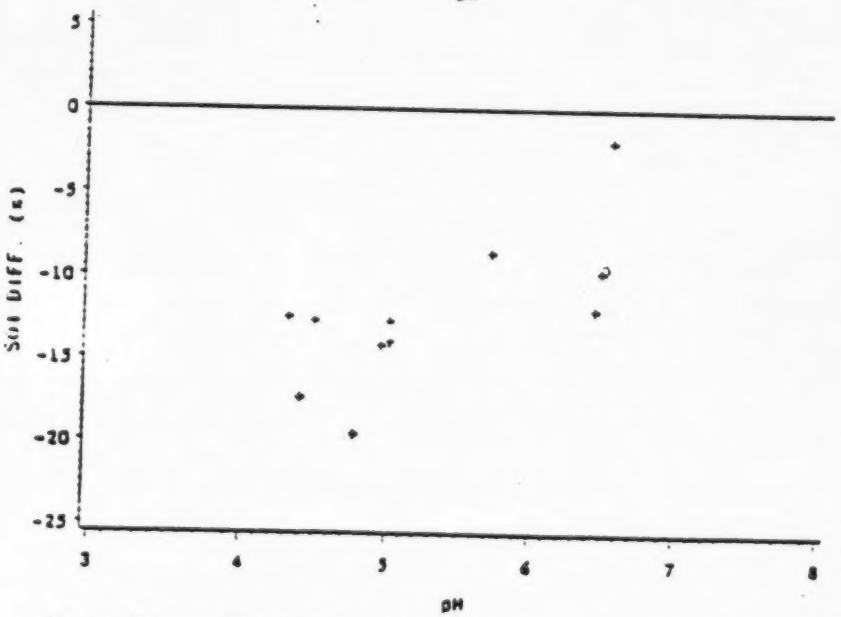


Figure 6-41. Effect of pH on (a) sulfate audit sampled for January - March 1988, and (b) for March 1988 OEN precipitation sampled reanalyzed in October 1988. SO_4 difference is:

(a) 100 (Measured SO_4 - Designated SO_4)/Designated SO_4

(b) 100 (March SO_4 - October SO_4)/October SO_4, where October sulfate is assumed to be correct.

with one exception, were greater than those shown by the previous audit results.

To examine the effect of sulfate concentration on the percent error, we present the data in Figure 6-42. The audit results, shown in (a), do not appear to be dependent on sulfate concentration. The data grouped around zero error are for pH above 5.0, and the points in the 13 to 23% error range are for points below pH 5.0. In contrast, the OEN data show an increase in sulfate percent error with sulfate concentration. The four points with smallest error, at -1.9 to -12.0%, are for the samples of pH above 5.1. The discrepancy in results between the audit and OEN sample data may be indicative of changes in the ion chromatograph malfunction.

An attempt was made to determine a method to "correct" the measured audit data. The only method which showed promise was based on the relationship between the error in sulfate and the hydrogen ion concentration of a sample. An adjustment was developed in the form:

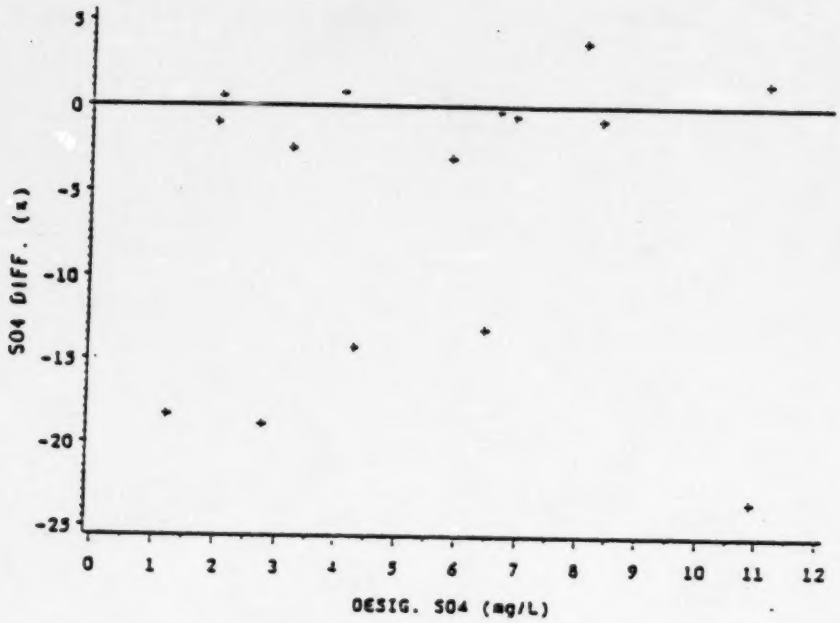
$$\Delta SO_4 = k\,[H] \qquad (6\text{-}18)$$

where:

- ΔSO_4 is the error in the sulfate (mg/l), i.e. designated minus measured values
- k is a constant (dimensionless)
- $[H]$ is the hydrogen ion concentration (mg/l)

The quality control check samples (QCCSs) used were neutral, and an adjustment of this form would reflect the fact that the QCCSs showed no errors. A linear least-squares fit gave a value of 9.9 for k, with an r-squared of 0.89. This fit encouraged the belief that this adjustment modelled the malfunction adequately. The adjustment was developed from the data alone, and has no obvious physio-chemical basis.

(a)



(b)

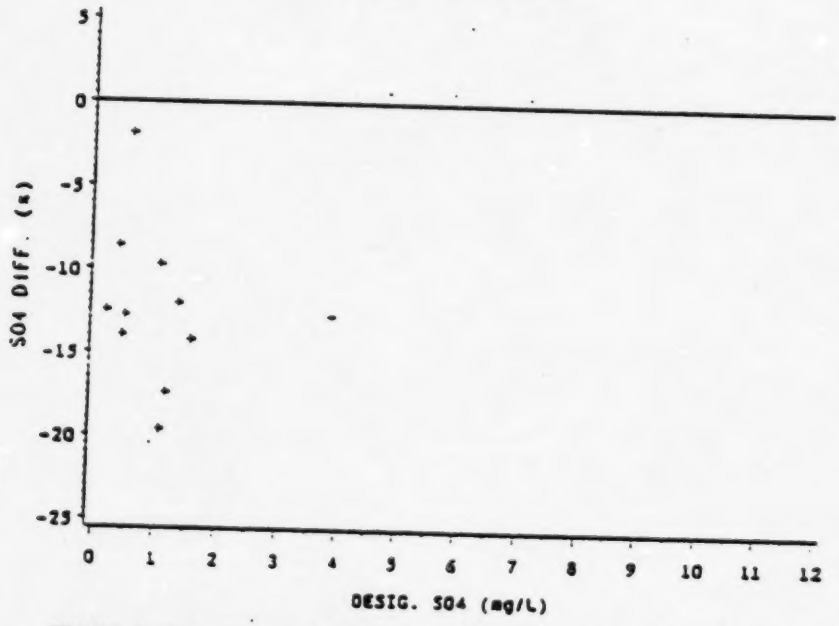


Figure 6-42. Effect of sulfate concentration on measured sulfate for (a) audit samples analyzed in March 1988 and (b) for CEN samples first analyzed in March 1988 and reanalyzed in October 1988. SO_4 difference is:

(a) 100 (Measured SO_4 - Designated SO_4)/Designated SO_4.

(b) 100 (March SO_4 - October SO_4)/October SO_4, where October SO_4 is assumed to be correct.

To test how well the adjustment performed on the rainwater sample data, the charge balance was calculated for samples both with and without the adjustment. Figure 6-43 shows the distribution of charge balance, expressed as the 25th, 50th and 75th percentiles of the sum of the anions minus the sum of the cations, for monthly collected samples in 1986 and 1987. The charge balance varies around zero for 1986 and for January 1987 through July but becomes much more negative for August through December, 1987. This behavior is due, at least in part, to a deficit in sulfate. The late July-August 1987 collection month corresponds to an analysis start date of October 26, 1987.

The charge balance behavior for samples analyzed on October 19 and 20, 1987, just before the presumed onset of the problem, is presented as squares in Figure 6-44. It can be seen that there is an almost even scatter of the charge balance around zero. In the same figure are plotted (by pluses) the charge balance for samples analyzed on December 23, and 24, 1987, when the malfunction appears to have been particularly severe. In contrast to the October data, the December charge balance shows a predominant anion deficit. Organic acids can contribute to this anion deficit but their presence is expected to be small in the winter (37, 38) since their origin is primarily from biogenic emissions from vegetation (39).

Attempts to adjust the data analyzed after October 20, 1987 using Equation 6-18 with $k = 9.9$ were not successful. The sulfate values for high concentrations analyzed on October 26 and 27 were over-adjusted while the December 23 and 24 data were under-adjusted. Thus, the adjustment factor developed from the audit samples and the retested OEN samples does not model the malfunction adequately. The adjustment cannot be used to salvage the data.

It would be possible to develop an adjustment factor for the sulfate needed to return any given batch of samples to a median charge balance of zero (or any desired degree of imbalance). However, such a factor would contradict the finding of no errors in the QCCSs,

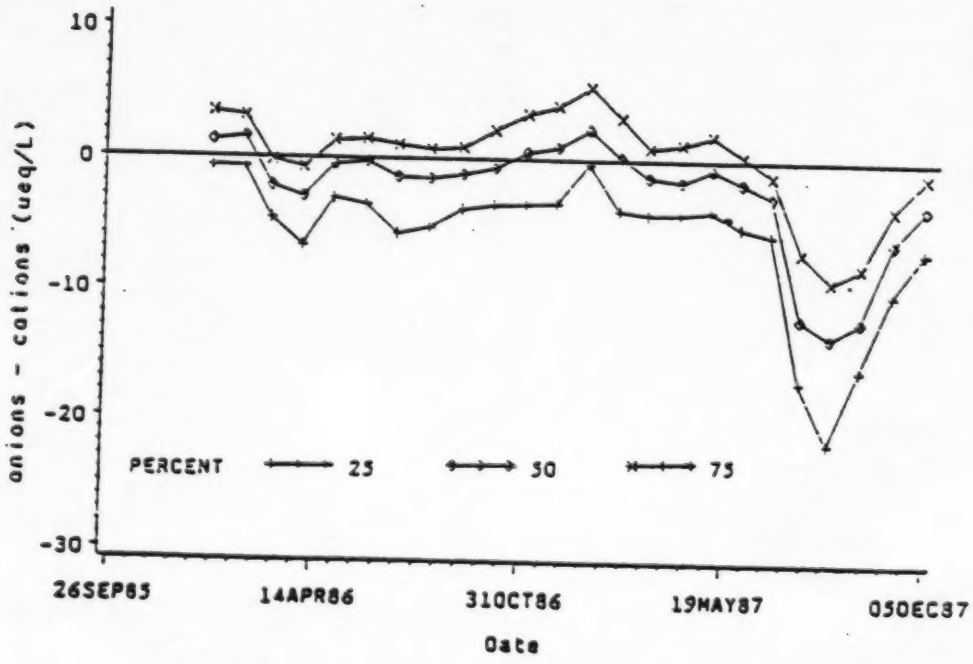


Figure 6-43. 25th, 50th, and 75th percentiles of charge balance (anions - cations) of precipitation samples for 1986 and 1987.

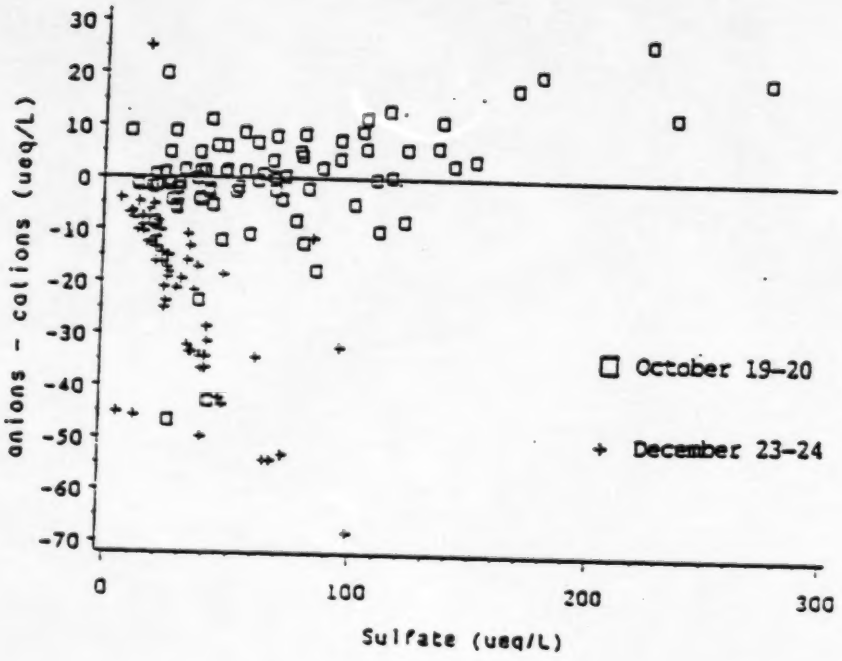


Figure 6-44. Charge balance (anions - cations as a function of measured sulfate concentration for precipitation samples analyzed in October 19 and 20, 1987 (before problem occurs) and on December 23 and 24, 1987 (when problem was severe).

since a blanket factor applied to all samples would change the QCCSs. Also, a perfect charge balance does not of itself imply that the instrument is performing according to specifications; the batch of samples analyzed on March 31, 1988, has a median charge balance of very close to zero, but an acidic audit sample analyzed on that day showed a sulfate error of over 20%. Further, the nature of the malfunction is unknown, thus hindering efforts to model it. As mentioned in the chronology at the beginning of this section, in early April, 1988, after all of the UAPSP samples had been analyzed, several components of the ion chromatograph were replaced as part of a scheduled service. One of the components was "green and gunky", suggesting a type of organic contamination. Since that time the performance of the instrument has been normal.

In summary, there was a malfunction of the ion chromatograph which appears to have begun on or about October 26, 1987, and to have lasted until all the UAPSP samples were analyzed. This period corresponds to samples collected between late July and December, 1987. Many of the sulfate measurements during this period were outside the specifications for laboratory accuracy, and should be used with extreme caution. The charge balance provides some guide as to the quality of an individual sample's chemistry.

Finally, based on the above findings, the sulfate problem may have been detected very soon after its onset by the use of quality control check solutions which simulate rain or at least were of pH 4.0 to 4.5 or by true spikes. It is thus recommended that such acid solutions be used for the QCCS in all laboratories performing precipitation analyses.

SECTION 7

Recommendation for the Identification, Coding and Use of TRACE Samples in the NADP/NTN Deposition Monitoring Program

David S. Bigelow
NADP/NTN Quality Assurance Manager
Natural Resource Ecology Laboratory
April 1989

Recommendation for the Identification, Coding and Use of TRACE Samples in the NADP/NTN Deposition Monitoring Program.

Background

At the NADP Technical Meeting held in Minneapolis in November 1987, a discussion concerning the use of trace samples in data summaries resulted in a recommendation by Subcommittee 3 to disallow the use of the event pen as an indication of trace precipitation. It was further recommended that the amount code TRACE be eliminated from the daily rain PRECIPITATION TYPE on the Field Observer Report Form (FORF). The argument for such a change in field procedures was based upon the belief that a weekly precipitation amount of TRACE can only be justified after carefully examining the weekly rain gage chart and FORF, AND that this judgement should only be made at the Central Analytical Laboratory. Daily trace amounts should only be based upon personal observations and since most operators were not 'in residence', the determination cannot be made.

Last year, at the NADP Technical committee meeting in Champaign, presentations to subcommittees includes discussions of the effect low volume samples can have on sample invalidation criteria. Based upon these discussions and a subcommittee recommendation, the Coordination Office revised the definition of a valid trace sample for the purpose of computing completeness criterion #1. Noteworthy of the discussion was the definition of a trace sample as $<.02$ inches of precipitation as measured on the Belfort rain gage, or, its bucket equivalent.

The discussions of the above two trace sample issues point out, what I believe to be, a three-part problem that results in the inconsistent treatment of trace samples in the NADP/NTN monitoring program. The following discussion will hopefully clarify the problems and offer specific recommendations.

Definition and Use of a TRACE Samples in the NADP/NTN

In the philosophical sense, the network has agreed that a sample coded trace should be a wet deposition only sample, that it not be the product of dew, frost, fog or other types of condensate, and that it represent an amount of precipitation that is below the detection limit of the sampling system. In implementing this philosophical definition, the network uses a number of operational definitions to identify trace samples in its data management operations. I have attempted to present all of these operational definitions in the following table. Definitions listed in the table seem to form reasonable method for identifying TRACE samples in network data. However, the method begins to break down when the network attempts to differentiate TRACE samples from non-precipitation events and when it attempts to estimate 'true' sample volumes and rain fall amounts.

Statement of the Problems

Part of the problem in identifying and processing trace samples stems from the network's reliance on the Site Operator to initially identify and sometimes sum trace samples. Another part of the problem can be attributed to the networks practice of accepting two different measuring devices for the determination of precipitation amount. And yet a third problem arises because of the data processing required to integrate the operator's observations, chart interpretations, and bucket volumes in light of the philosophical definition of a trace sample that the network has adopted.

Table 1 NADP/NTN Definitions for Trace Amounts of Precipitation

	Situation/ Definition	Method of Detection	Daily Rain inches	gms Bucket Equivalent
Field Operations:				
	Operator Does Not Interpert Chart < .05inches			
1.	Event pen indicates collector opened, small unreadable amount of deflection on the rain gage chart (less than 0.05in), personal observation by operator	Chart, Event pen, Observation	T	< 86
2.	Event pen indicates collector did not open, small unreadable amount of deflection on the rain gage chart (< .05in), personnel observation	Chart, Observation	T	< 86
3.	Event pen indicates collector did not open, no indication of precipitation from the rain gage chart, only observered by operator	Observation	T	> 0
4.	Event pen indicates collector opened, no indication of precipitation on the rain gage chart, personal observation by operator	Event pen, Observation	T	> 0
	Operator Does Interpert Chart			
5.	Event pen indicates collector opened, small unreadable amount of deflection on the rain gage chart (operator believes amount to be below 0.025 in), personal observation by operator (Above (1.) without personal observation)	Chart, Event pen	0.01	17
6.	Above (2.) without personal observation	Chart	0.01	17
7.	Event pen indicates collector opened, no amount of deflection on the rain amount pen	Event pen	T	> 0
8.	Therefore for weekly sample amounts (7X)		T-.07	0-121
or	Worst Case (7X)		T-0.28	0-483
Laboratory Operations:				
9.	A *bucket volume* arriving at the laboratory with approximately 10 mls or less of liquid. These samples are not analyzed.	laboratory technician weighs incoming bucket	< 0.006	10

	Situation/ Definition	Method of Detection	Daily Rain inches	Lab Type
Data Management:				
10.	weekly precipitation coded TRACE (-7.00), bucket volume is 0	one half the DL of the Belfort	0.005	da
11.	weekly precipitation coded TRACE (-7.00), bucket volume is 0-10	one half the DL of the Belfort	0.005	t
12.	weekly precipitation coded TRACE (-7.00), bucket volume is $>$ 10	one half the DL of the Belfort	0.005	w/wa
13.	weekly precipitation changed to Missing (-9.00), bucket volume is 0		Missing	da
14.	weekly precipitation changed to Missing (-9.00), bucket volume is 0-10	substituted Bucket Volume	0.001-0.006	t
15.	weekly precipitation changed to Missing (-9.00), bucket volume is $>$ 10	substituted Bucket Volume	$>$ 0.006	w/wa
16.	weekly precipitation coded 0.01 to 0.02, bucket volume is 0	Operator	0.01-0.02	da
17.	weekly precipitation coded 0.01 to 0.02, bucket volume is 0-10	Operator	0.01-0.02	t
18.	weekly precipitation coded 0.01 to 0.02, bucket volume is $>$10	Operator	0.01-0.02	w/wa
19.	weekly precipitation coded $>$ 0.02, bucket volume is 0	Operator	$>$ 0.02	da
20.	weekly precipitation coded $>$ 0.02, bucket volume is 0-10	Operator	0.01- 0.02	t
21.	weekly precipitation coded $>$ 0.02, bucket volume is $>$ 10	Operator	$>$ 0.01	w/wa

Operator's Procedures

I do not disagree with the premise that the identification of trace samples, either for daily amounts or weekly amounts, is best done centrally. I do believe however, that the operator's opinion is as an important of a clue as is the opinion of a data manager. I further believe that the elimination of the **T** code on the FORF and the elimination of the use of the event pen to 'alert' the data manager to 'potential' trace events will reduce the amount of readily available information upon which the data manager and perhaps others, can base their judgement. I am especially concerned because of the network policies which prevent the examination of each rain gage chart by CAL.

I recommend that field procedures for Operators remain unchanged and that they be allowed to use all means available to them to estimate the occurrence of and amount of volume associated with a daily or weekly TRACE amount of samples liquid.

Acceptance of Two Different Devices for Measurements of Volume

The practice of using the bucket volume in lieu of a rain gage volume in those instances where rain gage measurements are either not available or have been invalidated must continue. This practice has accounted for as much as a 12% reduction in the number of invalid samples in the network on an annual basis. Making this substitution for all TRACE samples, however, might improve the quality of the TRACE and other low volume sample amounts in the NADP/NTN data. The improvement would be the result of the bucket volume being measured on a finer scale (1-69 division units as grams) than the rain gage (0-4 one hundredths divisions as inches). Support for this recommendation comes from an examination of the simple averages of low volume ($<$ 0.05 inch on the Belfort) precipitation amounts, bucket volumes and collection efficiencies for all non-zero low volume samples. These averages indicate that certainly for Lab type *w* samples (40%) the rain gage is under estimating precipitation. I suspect that Lab type *t* and *wa* samples also have underestimated rain gage values since the rain gage amounts for these two types are not very different from each other or from the other Lab type.

Table 2

LabType	Rain Gage Amount	Bucket Volume	Catch Efficiency	n
qa	0.03	50.0	0.969	115
t	0.02	7.8	0.296	615
w	0.03	62.6	1.27	1499
wa	0.02	21.58	0.701	1526
	0.02	36.1	0.87	3638(3753)

I recommend that all TRACE samples, defined as those below 0.05 inches on the Belfort, use the AeroChem Metrics bucket volume as the official weekly precipitation amount for the purposes of data summaries that span multiple NADP/NTN sampling weeks.

Data Processing Problems

Data processing problems involve two basic issues: Is the sample a wet deposition sample?, and, should the chemistry be included in a weighted average? Based upon the uncertainty of the Operators ability to identify trace amounts as wet deposition-only samples versus dew, fog, etc; the fact that we do not explicitly ask him to differentiate among these types; the fact that these types of events are beginning to be treated as neither wet not dry deposition but as some new yet undefined portion of deposition, I would argue that we have no business including them in our estimates of wet deposition.

I recommend that all samples of less than 70 grams bucket volume that are recorded as less than 0.05 inches on the Belfort AND that have chemistry values be reported as a separate weighted average and deposition amount by the network. The samples would be designated as Low-Volume Trace Samples.

SECTION 8

Straw Man Data Quality Proposal for Coding Daily Rain Values Collected by the NADP/NTN Monitoring Network

David S. Bigelow
NADP/NTN Quality Assurance Manager
Natural Resource Ecology Laboratory
April 1989

Straw Man Data Quality Proposal for Coding Daily Rain Values Collected by the NADP/NTN Monitoring Network

D.S. Bigelow
April 1989

Current Practices:

- CAL removes daily rain values from sample records transferred to the Coordination Office and from field forms by crossing out the values prior to their submission to data entry personnel. This procedure is implemented when:
  a) The rain gage is suspected to be out of calibration.
  a) The rain gage is suspected of having a zero offset problem.
  b) The rain gage is suspected of having a stuck pen.
  c) The rain gage has a clock problem.
  d) The rain gage has not been winterized.
  e) The rain amount values are from a non-approved rain gage.
- The Coordination Office attempts to 'recover' this information by requesting the CAL to send the values that were recorded on FORFs and to send the reason they were deleted.
- Oftentimes the CAL Data Quality Control Officer is able to include this information with the other notes passed along monthly to the Coordination Office as a part of the routine transfer of data from the CAL to the Coordination Office.

Minimal Proposals:

A. CAL not delete daily rain records FORFs. The network should not be deleting data from network records. Daily rain records are the only type of information currently being handled in this manner.

B. CAL and the Coordination Office implement screening level, sampling protocol or some new category of codes which more easily identify undesirable daily rain values. Since CAL has already identified some cases where it believes daily rain values are not representative of the network, I would propose these cases be the first to be coded. I suggest:

nw=	Rain Gage not winterized.
nc=	Rain Gage out of calibration because of one or more of the following: zero offset, stuck pen, linear sensitivity.
rc=	Rain Gage clock problem.

C. Since CAL also currently acknowledges rain fall amounts from collocated gages in certain instances, I suggest adding the following codes to the above list:

es =	Estimated from a collocated approved rain gage.
ex =	Estimated from a non-approved collocated rain gage.
c# =	Rain value is an accumulation from the previous # days.